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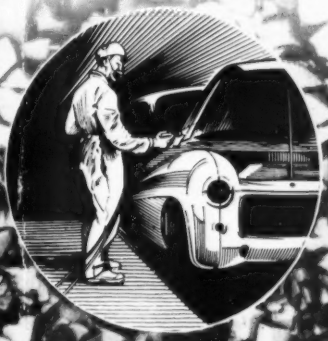

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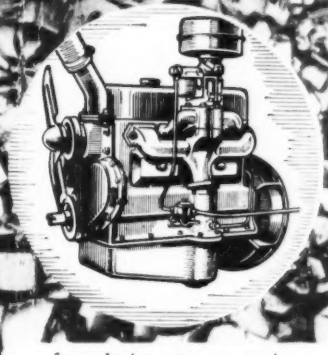

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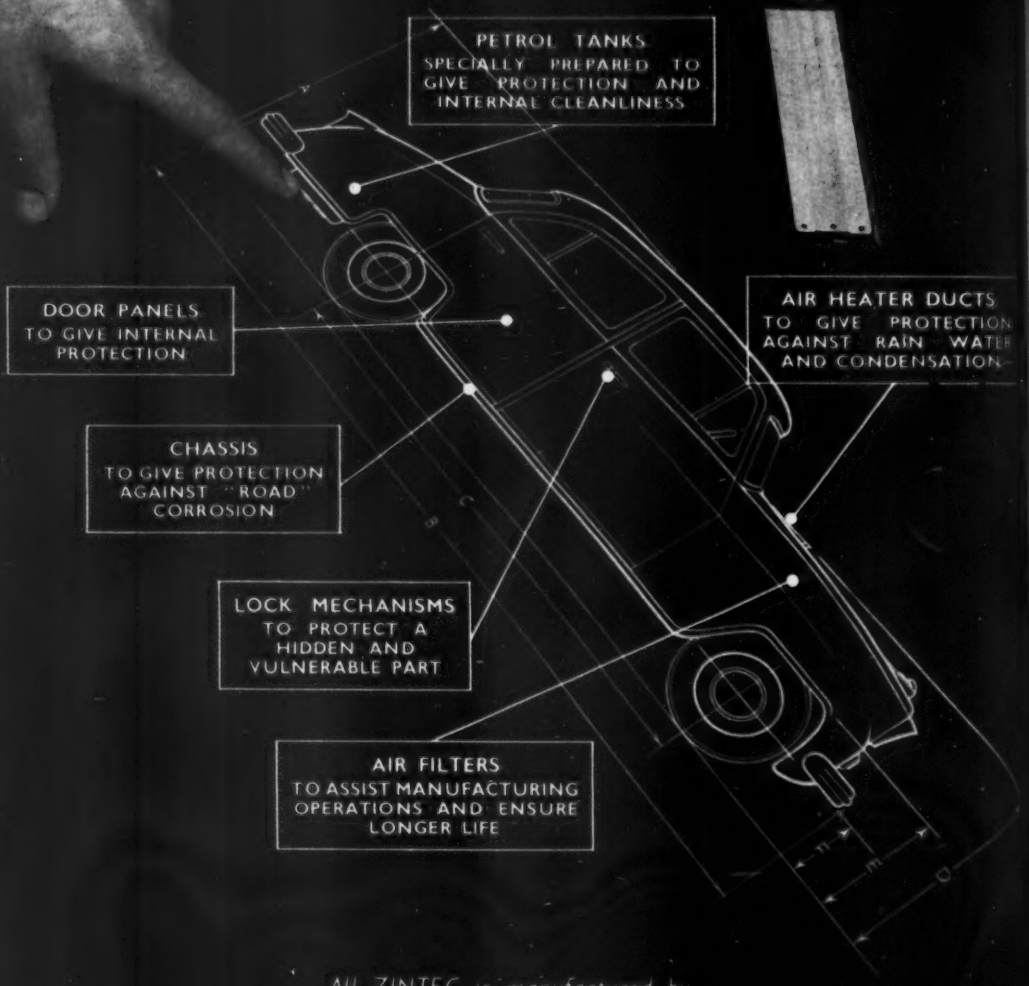
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THIS JOURNAL IS DEVOTED TO THE SCIENCE AND TECHNOLOGY OF PAINT APPLICATION, ELECTRODEPOSITION, VITREOUS ENAMELLING, GALVANIZING, ANODIZING, METAL SPRAYING & ALL METAL FINISHING PROCESSES. THE EDITOR IS PREPARED TO CONSIDER FOR PUBLICATION ANY ARTICLE COMING WITHIN THE PURVIEW OF "METAL FINISHING JOURNAL" AND ALL SUCH ARTICLES ACCEPTED WILL BE PAID FOR AT THE USUAL RATES.

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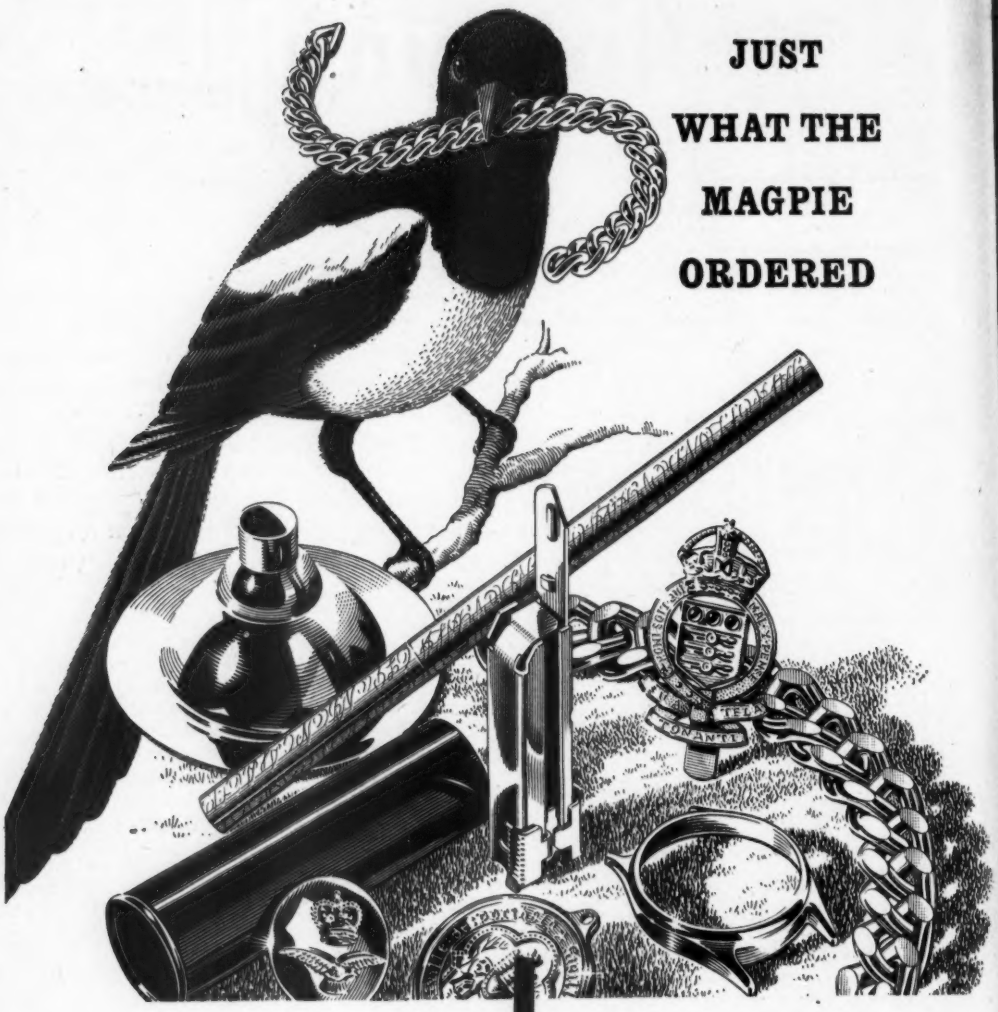

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COUNTING THE COST

THE determination of anything approaching an exact figure for the cost of manufacturing or processing a component is a matter of considerable complexity involving as it does the consideration of so large a number of variables, unknowns, and optional charges. Certain manufacturing processes are of such a nature that they lend themselves to a more or less exact analysis of cost, while others are very much more refractory from this point of view.

The electroplating process has always been one which has presented considerable difficulties in the way of accurate cost analysis, and for various reasons this has been particularly the case where the plating shop is a department, and usually a minor one, of a large manufacturing organization. This can be accounted for to some extent by the wide variety of components which are customarily processed in such plants and by the considerable variation in thickness and prime cost of deposited metal. Again, because of the fact that very large quantities of small components are involved, barrel plating is an even more complicated subject for costing than is still-vat plating.

Although cost accounting is a generally acknowledged and skilled profession, the criteria upon which cost calculations are based are still far from standard and vary quite considerably between different companies. However, the quotation of a real price for a job by a plating concern to a prospective customer, must have as a necessary pre-requisite the determination, within reasonable limits of accuracy, of the actual works cost of carrying out the job. In practice it is found that the quotations from different firms can vary for a particular job more widely than could be justified by differences in overheads and productive efficiency, which would indicate that the methods of costing used by those whose quotations vary widely from the norm, have not been wholly realistic.

Further evidence in support of this view can be drawn from a consideration of the price quoted in relation to the weight of a particular metal which is required to be deposited. It is not unknown for the actual price of the metal deposit, assuming that the specified thickness of deposit is maintained, to account for such a large proportion of the price quoted as to leave a ridiculously small sum available to cover overheads, direct labour, profit margins, and other necessary charges.

The quotation of a price so uneconomically low as to return either no profit or a direct loss does sometimes appear justified as a means of obtaining a first order in the face of keen competition, but it is a practice which is undesirable on a number of counts. One of the most important reasons for deprecating this course of action, is that it leads to undesirable economies in the actual plating process, which all too often result in the production of an inferior finish and consequent loss of good will, not only for the firm concerned, but frequently for the industry as a whole.

Furthermore, the customers of the electroplating industry are not entirely unaware of the basic costs involved in the deposition of a coating, and they are showing increasing realization of the fact that frue value for money is seldom obtained by paying a price which has been cut to a level which is a prima facie *economic absurdity.*

Finally, there is in this a lesson for those responsible for the costing of plating departments of large organizations. It is often argued that the elimination of the profit margin of an outplater by setting up an internal plating department must result in lower costs, and inadequate costing systems often fail to reveal the fallacy in such a contention.

The adoption of soundly conceived costing methods based on standard criteria would go far towards enhancing the reputation of the electroplating industry which has not been completely untarnished in recent years. It is a subject to which one or other of the representative bodies might profitably give some thought.

Talking Points by "PLATELAYER"

TOPICAL COMMENT FROM THE MAIN LINES AND SIDE LINES OF METAL FINISHING

SEQUESTRATION

GREAT things have been expected in the plating industry from the so-called sequestering agents. These, as is well known, are substances which are able to suppress the ionic form of metallic compounds while keeping them in solution. They are usually complex organic materials, particularly the ethylene diamines such as ethylene diamine tetra-acetic acid and a host of related substances.

In electroplating these products can be used in various ways. When included in alkaline and electrolytic cleaner formulations they can prevent the re-deposition of dissolved metals, and they should also theoretically reduce the susceptibility of bright nickel solutions to metallic contamination by keeping heavy metals in non-ionized form. These applications seem reasonable, although other suggestions such as the use of solutions of chelate compounds in place of cyanides for plating baths or for producing bright deposits are more problematical.

There is, however, an understandable resistance on the part of many people who should know something about plating to the concept of allowing concealed metallic impurities to be present in plating solutions even if they have been rendered innocuous. After all, a change in operating conditions such as temperature or *p*H can easily cause the impurities to revert to the ionic form with disastrous consequences, while unestablished possible side-effects of the sequestering agents themselves are not out of the question.

Yet the demand for plating solutions which are less susceptible than those currently in use for electroplating is considerable, and the sequestering agents may be well worthy of further investigation on this account. This again, is a case where research might pay useful dividends.

CAVEAT

INDUSTRIAL hazards, and particularly accidents occurring in the handling of chemicals, are extremely difficult to guard against, particularly because surprising things happen from time to time. It is therefore very necessary that experiences of such risks should receive the widest publicity to warn others who might be tempted to do the same thing. This is why the quarterly report "Accidents" published by H.M.S.O. is so useful, despite the fact that someone once said that there was no such thing as a preventable accident, because if it could be prevented or foreseen it was not an accident!

A typical example of a surprising effect was recently reported where trichlorethylene was added to a highly inflammable solvent used for extraction purposes in order to reduce the fire hazard. After a time the mixture began to give off bubbles of gas which ignited spontaneously, and the resulting fire was only put out with difficulty. The material being extracted had been made alkaline with caustic soda, leading to the formation of trichloracetylene, a gas which ignites or explodes spontaneously on contact with air.

HOW TO GET A RISE

MANY professional bodies now have periodic remuneration surveys which take the form of questionnaires which members are asked to return anonymously giving particulars of their age, earnings and the like. The figures are then analysed and tabulated and the results published. The Royal Institute of Chemistry, which recently completed its latest survey, always gets a good response, no less than 76.7 per cent. of the cards issued to more than 12,000 members being returned on this occasion. An interesting subject for speculation is why the Institution of Metallurgists in a similar survey has only succeeded in obtaining data from some 50 per cent. of its members.

This brings us to the question of what use the recipients are to make of the data supplied. Presumably those who are paid less than the average will use the reports to press their employers for an increase, whilst those who get more will keep very quiet. One must assume, of course, that no substantial proportion of people answering the questionnaires exaggerate their pay to step up the average, but technicians are an honest group as a whole so that the assumption is a fairly safe one.

A subject of as much interest as the actual pay-packet size, however, is the question of how the recipient got it. To this end the sponsors of the next survey might include some such pertinent questions as the following:

(1) When did you last receive an increase?
(2) Did you have to ask for it, or was it offered?
(3) Would you threaten to resign if an increase was refused on request?

Such surveys are, I suppose, needed because in this country we tend to be secretive about our pay—a recent investigation showed that even quite a large proportion of wives do not know the size of their husbands' pay packets. Yet in some Scandinavian countries a register of all income tax returns is open to the public, while many American Corporations publish the salaries of their executives. Nobody seems to be embarrassed by these disclosures.

BRIGHT NICKEL PLATING

The Reaction Mechanism of Brighteners for Nickel Plating Baths

by Dr. I. R. BELLOBONO *

THE excellent baths which are commercially available for electroplating with bright nickel have been developed by a procedure much more akin to an art than to a science. Apart from surface-active agents or anti-pitters, for which it is fairly simple to formulate a physical and chemico-physical theory in respect of their actions, there has generally been a very poor degree of scientific understanding of the interactions of the organic compounds which are usually added to bright-nickel plating baths.

The *chemical nature* of the brighteners can be extremely varied and, in general, many of them can provide colloidal solutions or suspensions which tend to induce the microcrystalline structure of the deposit. The colloidal particles arrive at the cathode surface and there influence the precipitation of the metal, inhibiting and hindering, by the formation of a large number of foci of crystallization, the formation of large crystals. Intervention of the colloids must not go beyond the contact surface between the electrolyte and the metal. This assumes a compact form having a density very close to that of cast metal. With colloids penetrating into the interior of the deposit and not remaining in the catholyte, a porous metal or a "carpet" of minute crystals which, in either case, would not be satisfactory from the technical point of view, would be obtained.

The theories relating to the actions of the chemical reagents concerned in the electrodeposition of nickel can be divided into five main classes, which although arbitrary, are often convenient, particularly as a simple means of setting out experimental facts.

The Theory of Reducing Action

In chronological order, this theory is the oldest of all(1). At the period in which researches were being undertaken on the basis of A. Betts'(2) observations, this theory was postulated by Kern(3).

Beneficial action would be conferred by substances having reducing power. Glaser(4) had noted that reducers in some cases avoided spongy deposits. There was not much basis for such a theory from the chemical point of view and Betts(5) noted that pyrogallol, which is fairly useful, for example, in electroplating lead, while reducing copper salts, did not reduce lead salts. Most of the useful reagents certainly do not possess any reducing power under the conditions in which their action occurs.

Theory of Adsorption

The phenomena being discussed have repeatedly been ascribed to adsorption of the colloids or of the reagent applied to the surface of the cathode. The theory is assumed to be axiomatic by W. Bancroft(6) and W. Blum(7), but they did not investigate deeply the mechanism operating the action of adsorption nor did they concern themselves with all the consequences to which the theory could lead. The basis of these views is the general observation of the influence exerted by quite small quantities of additions of alien substances, quantities insufficient to explain considerable chemical effects in the interior of the bath itself. This hypothesis of the formation of an adsorption film on the surface of the cathodes, formed of additions to the electrolytes, has by now been experimentally confirmed(8).

There is also the adsorption of the *inhibitors* themselves. Mathers and Leible(9) have studied the adsorption of various essential oils on to strips of metal and have noted that adsorption increases in the order:—Pb, Sn, Cu, Cd, Zn, Fe, Ag. This order is identical with that of the difficulty in effecting compact deposits by adding these same oils. The rate of crystallization becomes slowed down *i.e.*, there is a reduction in the number of nuclei, because the metal no longer precipitates by an ordinary mechanism of solidification or saturation, but by reason of the current which discharges the ions from the metal and causes it to precipitate in the microcrystalline state.

Metals usually precipitate in a compact form on the cathode from electrolytes containing complex ions of the $[Zn(CN)_4]^{2+}$ type, which represents, in other words, an extreme dilution of the metallic action which is discharging. A similar cause may be ascribed to the film-like stratum adsorbed on the cathode in such a way that a steep gradient in the ion concentration of the nickel is brought about. Its efficacy or otherwise could depend on the degree of steepness of the actual gradient.

According to this, the film of adsorbed material would affect the deposit because of the reduced

* *Based on a series of articles published by the Italian journal Galvanotecnica. This English version is reproduced with the collaboration of the editor and the author of the work.*

concentration of metallic ions in the stratum adjacent to the electrode. This theory, while providing for the existence of the cathodic film, which is of great importance, does not provide an explanation of the phenomenon of deposition in its actual essence, for no explanation is given as to why some substances act as inhibitors and give a cathodic film which slows down the migration of the nickel ions.

Theory of Complex Ions

The chemical reagents appear to act through the formation of complex ions which intervene in the process of cathodic deposition. According to this theory, electrodeposition is based on complex ions, for example $[Zn(CN_4)]^{2+}$ Isgarischen[10] noted the formation of complex cations of zinc, copper and gelatine. The growth of the crystals of the metal appears to be retarded because the rate of separation of the free metallic ions from the complex is relatively low.

With large dilutions of brightener it is impossible to confirm this action in the interior of a bath because a few complex ions would always be forming. It would, however, be statistically improbable that these few, in approaching the cathode, could vary the progress of deposition of the other non-complex ions present, forming as they do the great majority.

Theory of Preferred Orientation of Nickel Crystals

Brighteners, in addition to affecting the grain-size of the crystals, which can be precipitated in sizes smaller than 0·00001 mm., can also affect the growth of the crystals themselves along a given spatial orientation[11] or can regulate particular internal stresses by a local raising of the *p*H[12].

This theory was studied and thoroughly investigated[13], particularly by F. Denise and M. Leidheiser[14], but this work, unfortunately, did not lead to any positive results. The last-mentioned authors worked with an ordinary Watts-type nickel-plating bath with 29 different organic materials. The compounds differed in their ability to affect grain-size in the nickel deposited and the type of preferred orientation stimulated. In the absence of organic additions and under the working conditions adopted by previous authors, the Watts bath provided a deposit with preferred orientation (100). A similar orientation had already been reported by other investigators[15].

It is noted, however, that when it is deposited on single crystals of nickel or copper, the deposit also appears in the form of a single crystal on the (100) face[16]. The explanation of this phenomenon is rather complicated. Small quantities of organic compounds can change the orientation and 23 of the 29 compounds examined in Leidheiser's work had a pronounced effect in lowering the grain-size of the deposit or in changing the type or degree of preferred orientation as compared with those obtainable with the unmodified Watts bath. A group of these materials produced a deposit with grain-sizes of over 10^{-2} mm. and with (100) orientation. They accordingly did not radically change the action of the Watts bath and did not provide a satisfactory bright nickel deposit.

A second group produced grains of nickel larger than 10^{-2} mm. with an orientation different to (100). A third group reduced them to a size of less than 10^{-2} mm. leaving its (100) orientation unmodified. Finally, a fourth and a fifth group reduced the (100) orientation or eliminated it altogether.

From an examination of the experimental results, it was deduced that no definite correlation exists between the brittleness of the deposits and the grain-size of the crystals. A grain-size above 10^{-2} mm. did not necessarily confer ductility and one below 10^{-2} mm. did not always impart brittleness. There did not even exist any correlation between the orientation and the brightness of the crystals. In any case, it was observed that another portion of the deposits (computed to be about 50 per cent. in the investigation) which exhibited brightness had no perceptible definite orientation.

Although it appears to be true that this portion did not exhibit any preferred orientation, it is also true that its absence did not necessarily lead to a bright deposit. A clear example of this is the deposit which Denise and Leidheiser obtained by adding 1-naphthylamine and 4-8 disulphonic acid; The specimen was bright in one part and dull in another. Nevertheless, the X-ray diffraction photographs of both areas were identical and it was concluded that the crystals were of a size between 10^{-2} and 10^{-4} mm. On the whole, however, as was also observed by Zentner, Brenner and Jennings[17], most bright-nickel deposits have small crystals, below 10^{-2} mm. in size.

The lack of preferred orientation in a large area of the deposits has been interpreted as being due to the operation of the organic agent which has the function of minimizing the differences between the crystal faces at the cathode surface. In this way, the growth of the crystal would no longer be controlled, during deposition of the bright nickel, from the surface of the nickel itself but from a film adjacent to the surface; for it was observed that when the reaction rate is controlled from the surface the reaction proceeds at different rates on the various crystal faces.

H. J. Read and R. Weil[18], however, found a complete lack of any correlation between crystal size and hardness and brightness of the nickel. Nevertheless, even they found an increase in hardness and a lowering of grain-size (these were checked by the electron microscope) when the brightness was increased, but in a manner very far from providing a general equation.

Theory of Increase in Cathode Potential

Although no interdependence between grain-size and brightness of nickel emerged from the above-mentioned investigation by Denise and Leidheiser, they observed an excellent degree of correlation between the effect of the addition agents on the growth of the crystals and the effect of these same compounds on the cathode potential. The compounds which had no effect in changing orientation and grain-size in the nickel had a negligible effect on the cathode potential, while the compounds which lessened the crystal dimensions, and at the same time changed the type or degree of the preferred orientation, had an effect—sometimes moderate, sometimes marked—on the cathode potential.

The substances which interfered only moderately with the manner of deposition of the nickel, a phenomenon made detectable by a scarcely-perceptible effect on the cathode potential, were also capable of reducing the crystals' grain-size, but were incapable of changing the type of orientation. The substances capable of drastically affecting the cathode potential were, however, capable, on the contrary, of changing the grain-size drastically.

Before proceeding to a more detailed explanation of the systematic research, undertaken by C. C. Roth and H. Leidheiser, Junr.[19], on the relationship between brightness of the deposits and cathode potential at which nickel is deposited, other factors will be discussed.

The increase in cathode potential (the term "increase in cathode potential" is intended to indicate an increase in cathodic polarization; accordingly, this "increase" of potential must be interpreted in the "negative" sense in every case, or rather, in the more negative or cathodic direction) during the electrodeposition of nickel in the presence of organic molecules implies that the nickel is electrodeposited with more difficulty in their presence. It is necessary to supply additional energy in the form of a higher voltage to the nickel ions so that they may be able to form a deposit of metallic nickel at a specified current density. Four possible explanations of this effect exist:

(*a*) Change of *p*H of the cathodic film, produced by the addition agent;

(*b*) Change of concentration of the nickel ions in the cathodic film caused by complexing;

(*c*) Increase in the chemical resistance of the cathodic film, caused by the presence of organic compounds;

(*d*) Adsorption of the organic compound with resulting change in the facility with which it effects the process:

$$Ni^{++} + 2 \text{ electrons} \longrightarrow Ni \text{ (cryst.)}.$$

From experiments undertaken by various authors, it transpired that the cathode potential in an unmodified Watts bath with a fixed current density increased as the *p*H increased.

The same experimental evidence suggested, however, that the results obtained in the presence of organic agents could not be explained solely on the basis of an increase in *p*H in the cathode film.

In many cases this increase was too marked for it to be only attributable to the different *p*H in the vicinity of the metal surface. With agitation, the same effect on the cathode potential was obtained as was found when the concentration of brightener was raised. Agitation had no effect in an unmodified Watts bath or a bath containing compounds which had little or no effect on the cathode potential. As soon as the solution was buffered with boric acid (*p*H=4), it would have been expected that agitation could do nothing except maintain the *p*H at the surface of the cathode in the vicinity of 4, and very probably uniform. If the change of *p*H had been the cause of the rise in potential, the latter would have had to diminish and not increase as a result of agitation. Later evidence includes the following facts:

(*a*) Slightly acid compounds, like sulphonates and benzoic acid, increase the cathode potential.

(*b*) Similarly, basic compounds, like aniline or isoquinoline, vary in their effects on the cathode potential.

(*c*) The bases which are rather stronger, like ethylamine, piperidine and cyclohexylamine, have a negligible effect.

The change in *p*H is not the chief cause of potential rise although it is not entirely impossible that the effects of *p*H play some part or make some contribution to the overall process.

Many compounds used in the study of the subject under discussion have the particular feature of forming complex ions with the nickel in aqueous solutions. A lowering of the concentration of the nickel ions ought to have the effect of raising the cathode potential. But even here, agitation does not provide an explanation on the basis of complexes alone, according to Roth and Leidheiser.

Indeed, agitation would lessen the thickness of the diffusion layer of the catholyte and hence would favour a homogeneous concentration of nickel ions. Agitation should, therefore, lower the cathode potential, but this runs counter to experience. It may therefore be deduced that phenomena leading to complication pure and simple can have no more than negligible importance.

The results obtained with ethylene cyanohydrin, quinaldine, coumarine and pyridine at current densities of the order of 10^{-2} amp. per sq. dm., which represents a total current of approximately 10^{-3} amp., indicated that not even chemical resistance was an insignificant factor. Under these experimental conditions, the potential drop, IR,

ought to be negligible in view of the minuteness of the current passing. Nevertheless, there was usually obtained with these brighteners a rise in cathode potential of the same order of magnitude as that obtained with 1 amp. per sq. dm. Hence, the contribution made by the potential drop IR—according to the conclusions of Roth and Leidheiser—likewise could not be the main cause of the phenomena being investigated.

Roth and Leidheiser accordingly came to the conclusion that the change in cathode potential was caused by the adsorption of the organic compound on the cathode surface with a resultant change in the degree of facility with which the whole process of deposition occurs. They deemed it impossible to decide, however, whether the change in cathode potential is a result of interference with the transfer of electrons from the cathode to the nickel ions in solution which, because of this, deposit themselves in the metallic state, or as a result of interference with the crystal growth of the atoms of nickel which are discharged.

As already mentioned([20]), in view of the content of organic substances in the deposits, it may be deduced that these have a fundamental part to play in the strictly electrochemical process of depositing nickel ions, a part which scientific investigation must clearly express, at least in qualitative terms.

The comparative efficacy of the chemical groups in increasing cathode potential during the electrodeposition of nickel was established by Roth and Leidheiser in the following, descending, order: nitrogen in bicyclic conjugated rings; nitrogen in monocyclic conjugated rings; nitriles; aldehydes; amino- and nitro- groups; tertiary amines; sulphones; sulphonylamides; sulphonates; carboxyls; ketones; phenolic or alcoholic groups. All compounds containing but a single weakly acid group, like phenol, benzoic acid or the sulphonates, have only a slight effect on the cathode potential. Introduction of a basic group—like aromatic nitrogen, nitrile or amino-groups—into similar compounds increases the cathode potential. Introduction of a basic group has little effect when it is an ortho-type, but more effect when it is a meta-type and most effect when the para-type.

In the case of meta- or para-acid groups added to basic groups in the benzene ring, the effect of double-substituted compounds is intermediate between those of acid and basic mono-substituted compounds. Similarly, the effect of *p*-hydroxy-benzo-nitrile comes between the effect of phenol and that of benzo-nitrile, while the effect of *p*-amino-phenol comes between that of phenol and that of aniline and the effect of *m*-sulpho-nitro-benzene comes between that of benzene-sulphonic acid and that of nitro-benzene.

The effect of the brightener on cathode potential increases, however, for example, in a series of alkyl amines with the size of the molecule. Not all these phenomena, however, can be due to the size of the molecule. The saturated compounds piperidine and cyclohexylamine have a negligible effect, while the corresponding aromatic compounds pyridine and aniline have brightening properties. It sometimes happens that compounds of small molecular dimensions, such as thiourea, ethylenediamine and propionitrile, are much more active than compounds with larger molecules of the type of dodecylamine or tri-ethylamine.

In general, however, the compounds with higher molecular weights require lower concentrations to act as brighteners, while compounds of relatively low molecular weight require higher concentrations.

In most of the cases mentioned, Roth and Leidheiser found a fruitful correlation of the results in the concept of a "doublet of available electrons", this term meaning a pair of electrons of the molecule of a compound able to be divided up, by means of an association which can be, or not, accompanied by a chemical reaction, with the molecule of another compound.

In the case, for example of ammonia or an alkyl-amine, there exists a single doublet of electrons unshared with other atoms or groups of atoms. Since it is a general rule that a compound is more stable (or is at a lower energy level) when more of its external electrons are shared with other atoms or atomic groups, the doublets eventually liberated tend to be easily available for the purpose of attaining a thermodynamically-preferred configuration.

In the nitrile group there are three available doublets of electrons, while there is only one doublet available in a double link, in a carboxyl (ketone or aldehyde) group, in a sulphydric group or in a cyclic nitrogen atom. No doublet is available in an alcohol group.

Roth and Leidheiser observed that, in general, the compounds most active in raising the cathode potential were those which had the largest number of free electrons. The exceptions found in the case of structurally similar compounds, like N-ethyl-N-(β)-hydroxy-ethyl-aniline, N. N-di-(β)-hydroxy-ethyl aniline and di-ethyl aniline, were explained to some extent by the steric impediment which they put in the way of the atom of nitrogen and the groups bonded to it.

Significant treatment of these considerations lies mainly in supposing that the attraction of the organic compound to the surface of the nickel during electrodeposition depends in part on the presence in the molecule of electron doublets made available by interaction with the atoms of the metal.

The force of the attraction of the organic molecule at the surface or perhaps the area covered by the molecule on the surface, would seem to depend to a large extent on the above-mentioned doublets.

It is apparent that other factors to be taken into consideration could well be the shape and size of the molecule and the relative tendency of its electrons to interact effectively with nickel.

According, again, to Roth and Leidheiser, the increase in cathode potential necessary to produce brightening effects on the deposit varied between 14 and 97 mV. A good 70 per cent. of the substances examined, however, caused an increase of between 20 and 50 mv. This increase would constitute qualitative representation of the number of atoms of nickel at the cathode surface which are covered by the organic material. Since it was observed in the first place that in the majority of the compounds there was needed for the attainment of brightness in the deposit an increase in cathode potential of 20-50 mv., the authors suggested that for brightness it is necessary that a certain minimum proportion of nickel atoms should be covered. A good bright deposit can occur only when the concentration of brightener is sufficient to exceed this minimum proportional covering. Since, however, bright nickel plating is a dynamic process, the surface is continually being renewed and it is necessary continuously to provide new organic molecules to replace those lost either through decomposition or through occlusion in the deposit or through de-adsorption or through diffusion of the catholyte.

When considering the absorption phenomena discussed above, which are similar to what could occur in the gas phase, Roth and Leidheiser judged approximately that the minimum proportion of cover necessary amounted to little less than complete covering of the surface to a depth of one molecule.

Roth and Leidheiser also hoped from their study to establish a direct relationship between cathode potential and brightness, but they were able to draw from it several fundamentally *useful* observations. In particular, several commercial baths provided an increase in cathode potential of 30 mv. and no bright deposit is obtained without a corresponding increase in cathode potential. The fact remains however, that raising the cathode potential does not inevitably lead to a bright deposit. Compounds like benzaldehyde, aniline, 1,3,6-collidine, melamine and phenylenediamine considerably increase the cathode potential but are quite ineffective in producing a bright deposit.

From this it is concluded that if the rise in cathode potential has to be considered essential to the production of a bright deposit, it would be preferable to consider it as an effect rather than as a cause of the basic phenomenon which is the main source of the action.

Electrochemists are accustomed to dividing brighteners into two classes, "primary" and "secondary". "Secondary" brighteners are substances which can be added in relatively large quantities without imbuing the whole with properties harmful to the deposits but which, by themselves, are incapable of causing a perfectly bright deposit to develop.

"Primary" brighteners, on the other hand, are compounds which can arrive in the bath as additions in small, or even very small, concentrations without any harmful effects being produced; they are particularly suitable for brightening. The difference between the two groups appeared fairly clearly from the studies of Roth and Leidheiser. The secondary brighteners like benzene-sulphonates, saccharine and *p*-toluene sulphonamide, had the following characteristics in common:

(*a*) They were relatively inefficient in raising the cathode potential, which could rise to 15-45 mv. at low concentrations and only increased a little when the concentration of the secondary brightener was raised.

(*b*) The deposits were fairly bright (but not mirror polished) under certain conditions and did not tend to exfoliate (low internal stresses).

Primary brighteners, however, such as cyclic compounds containing nitrogen, nitriles, polyamines, had the following characteristics:

(*a*) They enormously increased the cathode potential, which went on increasing as the concentration continued to be raised.

(*b*) The deposits were mirror-bright and tended to exfoliate when the increase in cathode potential exceeded about 30 mv.

From this, therefore, it is deduced that a good commercial bath should not be too stimulative of increase in cathode potential, and this should be so in order to avoid those phenomena of brittleness and very high internal stresses which inevitably accompany too high a cathode potential.

Conclusions

The various theories, from the earliest to the most recent, which have been propounded in explanation of the inner mechanism governing the action of materials used for brightening nickel have been discussed. Particularly emphasis has been given to the influence of organic materials on cathode potential because it constitutes one of the most significant conclusions associated with this field.

Such a theory would be primarily based on the assumption that the governing factor in the production of bright nickel might be the possibility of the organic materials yielding electron doublets.

It is not true, however, that all bright-nickel baths include substances capable of yielding electron couples and of increasing the cathode potential; it is not true, conversely, that substances capable of

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A Review of Processes in Current Use for THE SURFACE TREATMENT OF TITANIUM

by H. RICHAUD ★

A Paper presented to the 6th International Mechanical Engineering Congress.

TITANIUM which, no more than ten years ago, was considered a rare metal, is now becoming an industrial material possessing, in conjunction with a low density (d=4·5), excellent mechanical characteristics and good corrosion resistance to the majority of chemical agents.

This corrosion resistance arises from the fact that the metal, like aluminium, is covered by an adherent film of superficial oxide. This oxide film is furthermore at the origin of the difficulties encountered in achieving adherent electrodeposited coatings on titanium.

The principal surface treatments for titanium, namely, pickling, anodizing and electrodeposition, will be discussed.

Pickling

Three pickling baths may be used. One of these, the Virgo process, makes use of a molten mixture of soda (approx. 96 per cent.) and sodium nitrate (approx. 4 per cent.). This process dissolves the titanium oxide without attacking the metal, but suffers from the disadvantage of requiring an operating temperature in the neighbourhood of 500° C.

Another method is to use a hydrochloric-hydrofluoric bath, whose composition is:

—hydrochloric acid, 22° Be.:
15 per cent. by volume.
—hydrofluoric acid (40 per cent.):
3 to 5 per cent. by volume
—water: balance

This bath operates at room temperature (20 to 25° C) pickling being complete in a few minutes according to the degree of oxidation of the titanium. This bath is very active, it attacks the oxide and the metal at the same time, and the treatment must be controlled in such a way as to prevent the formation of corrosion patterns on the metal surface. The pickled surface obtained is matt grey.

The third process uses a nitric-hydrofluoric mixture of composition:

—nitric acid, 40° Be.:
20 per cent. by volume
—hydrofluoric acid (40 per cent.):
1 to 3 per cent. by volume
—water: balance

for a few minutes at room temperature.

This bath is less active than the previous one, and it gives a smooth surface, light grey in colour, and of pleasing appearance. It is used for the treatment of lightly oxidized surfaces or as a finishing process, after preliminary pickling in a hydrochloric-hydrofluoric bath.

Anodizing

Before carrying out electrolytic oxidation it is advisable first of all to clean the surfaces of the items to be treated; for this purpose, degreasing by means of a solvent, for example trichlorethylene, followed by pickling in one of the baths previously mentioned, if possible the HNO_3-HF bath, so as to obtain a surface with the minimum pitting, is recommended.

Anodizing is carried out in a phosphoric or sulphuric medium. The author has carried out most work with sulphuric acid in an electrolyte containing 20 per cent. by weight H_2SO_4, 66° Be., at a voltage of 18 volts at 20° C. The film of oxide thus formed on the titanium varies in shade from yellow to violet in relation to the duration of oxidation. The violet shade is generally obtained from about 10-minute's electrolysis.

An investigation has been made as to whether this electrolytic oxide film possesses dielectric rigidity, as is the case of the aluminium-oxide film formed by anodization; dielectric breakdown voltage tests carried out for this purpose gave nil values in all cases even on strips oxidized at 18 volts for two hours. It would seem therefore, according to these results, that the anodic oxide films on titanium are not insulating.

On the other hand the titanium-oxide films are certainly porous or fissured for they retain greasy matter such as lanoline. This property is utilized in practice to avoid seizing of parts, for example in screwing.

In this case the titanium components are anodized for 20 to 30 minutes; the oxide film is then impregnated by immersion in a bath of lanoline at 90° C approx.

Electrodeposition

Among the work done on this subject, that carried out by William H. Colner, Morris Feinleib and John N. Reding(1), should be mentioned.

★ *Chambery Research and Physical Testing Department.*

The principal difficulty in the way of electrodeposition on titanium arises from the fact, that the metal is covered by a natural oxide film. It is therefore essential for the titanium to undergo some surface preparation intended to put it into a suitable state for coating with an adherent electrodeposit. As a result of tests two methods which give satisfactory results have been selected; these are the formation of an electrolytic zinc deposit or of an oxide film which act as retaining bases.

Electrodeposition on a film of electrolytic zinc

After degreasing by means of solvents and pickling, the article to be treated is made the cathode of a zinc-plating bath, whose composition is as follows:

—hydrofluoric acid (40 per cent.):	200 c.c.
—zinc fluoride:	100 gm.
—ethylene glycol:	800 c.c.

Electrolysis is carried out for between 5 to 10 minutes, at a temperature of 20 to 25° C, at 6 volts, or a current density of the order of 1 amp. per sq. dm. The anode is a graphite plate.

After this treatment the article is covered by a zinc deposit, which constitutes a good retaining base for most electrodeposits such as copper, chromium, nickel, brass, silver, cadmium, etc.

Electrodeposition by means of an intermediate anodic oxide film

In this case the article, degreased and pickled, is made the anode of a hydrofluoric-acid/zinc-fluoride/ethylene glycol bath, whose composition has been previously detailed. This anodic attack is continued for 10 to 20 minutes, at a temperature of 20 to 25° C, at 18 volts approx., or a current density of the order of 5 amp. per sq. dm. The article thus treated is then in a suitable state to be coated with an electrodeposit.

These two techniques of surface preparation enable electrodeposits possessing good adherence to be achieved on titanium.

Using these methods, deposits of, in certain cases, up to 40 microns of copper, brass, tin, cadmium, silver, nickel and chromium, have been obtained. The baths used for the formation of these deposits are the standard baths in use in electroplating.

As an example, heavy chrome-plating of titanium has been carried out under the following conditions:

—degreasing in trichlorethylene
—pickling in nitric-hydrofluoric for 5 minutes at room temperature
—rinsing
—anodic attack, in a hydrofluoric/zinc-fluoride/ethylene-glycol bath for 20 minutes at 18 volts at 20° C, or a current density of 5 amp. per sq. dm.
—rinsing
—chrome-plating in the standard bath of the following composition:

chromic acid	: 300 gm. per l.
sulphuric acid	: 3 gm. per l.
current density	: 40 amp. per sq. dm.
temperature	: 50 to 55° C
duration	: 30 minutes
thickness of deposit	: 15 microns, approx.

Electrodeposits on titanium are used particularly:

1. To prevent seizing, for example by depositing tin.

2. To facilitate pressing; this is usually the case with copper-plating.

3. For decorative purposes; the author has effected decorative chrome-plating of brilliant and uniform appearance. Treatment comprises the following operations: mechanical polishing; degreasing; cathodic attack in the mixture hydrofluoric acid/zinc-fluoride/ethylene glycol; brass-plating; nickel-plating and chrome-plating.

4. Finally it is worth noting an application which is of great practical interest, that is the brazing of titanium.

The brazing alloy is made up by simultaneous, or for preference successive, for greater ease, electrodeposits, on the articles to beassembled. The brazing of the assembled parts is then carried out by heating them, for example, by means of a torch or in a furnace.

This process is of interest for a metal like titanium which is susceptible to damage by oxidation or nitration and for which treatment must be carried out either under vacuum, or in an atmosphere free from the gases likely to contaminate the articles to be assembled.

As an example, relative to this application, the brazing of two sheets of titanium was effected by an alloy consisting of:

Silver : 60 per cent.
Copper: 32 per cent.
Zinc : 8 per cent.

This was deposited on the sheets by electrolytic means in successive layers of silver and brass under the following conditions:

—degreasing by trichlorethylene
—pickling in hydrofluoric-nitric for 5 minutes at 20° C.
—rinsing
—cathodic attack in the hydrofluoric-acid/zinc-fluoride/ethylene-glycol bath for 5 minutes at 6 volts at 20° C
—rinsing.
—brass-plating : 6 microns
—rinsing
—silver-plating : 8 microns
—rinsing

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Surface Treatment of Titanium

(*Continued from page* 11)

—brass-plating : 6 microns
—rinsing
—silver-plating : 7 microns
—rinsing and drying

The sheets were then placed one against the other with an overlap of 20 millimetres for example, and under a load, then heated to 800° C for 30 minutes approx.

In this way assemblies can be effected, having good mechanical strength which is of the order of 2 kg per sq. mm. of contact surface.

Conclusion

The principal surface treatments for titanium are pickling, anodizing and electrodeposition. Pickling may be carried out either in a molten soda bath, or at room temperature in hydrochloric-hydrofluoric or nitric-hydrofluoric media.

As far as anodizing and electrodeposition are concerned, it is sufficient to point out that these treatments are similar to those carried out on aluminium.

In fact, when made anodic in an electrolyte, for example, a sulphuric- or phosphoric-acid solution, an oxide film builds up on the titanium in proportion to time and this film is suitable for impregnation for example by greasy matter.

The retention of electrodeposits is effected after a surface preparation which consists of replacing the natural oxide film, either by a deposit of zinc, or by a layer of anodic oxide. These processes enable the achievement of adherent deposits which are used for decoration, for preventing seizing or for pressing, as well as for the brazing of titanium.

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Bright Nickel Plating

(*Con inued from page* 9)

providing such electron doublets can always and invariably produce bright deposits of nickel. Hence this postulate could represent a condition which is essential but not sufficient, in the sense that it is essential that the brighteners should have the ability to provide electron doublets but that this essential feature is not sufficient by itself to effect production of bright nickel. Some other restrictive cause must accordingly intervene. Theoretical and experimental studies are at the present time being undertaken by Professor Bertorelle on the subject of this "sufficient condition" and also with a view to formulating a chain of reasoning which may be an improvement on the theories hitherto formulated to account for the presence of bright nickel.

No theory, however complete, will really be able to include in its explanations all the experimental phenomena being studied, or to foresee and anticipate new facts and new acquisitions so that none escape its rigid confines. If this were so, it would, by that very fact, cease to be atheory and would become a law; it is known, however, that in science this does not invariably or easily come to pass. It is not every theory that can rise to *unassailable* generalizations; often, indeed, it harbours just those defects that will be the pretexts for those new criticisms which are the fertile seed of new theories and are, in any case, the living sap of science.

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VINYL RESIN COATINGS FOR STRUCTURAL STEELWORK

IN a paper given recently before the St. Louis Coating Society and published in the *American Painter and Decorator* C. G. Munger discusses vinyl resin coatings which, because of their toughness, flexibility, resistance to chemical attack and moisture, and other desirable properties, are being increasingly used in U.S. industrial plants. The author points out that there are a number of danger spots in all plants which should be carefully watched during the application of any coating. If these areas are recognized and given particular care during the application, a good result can be obtained; if not no coating, however good, will put up a satisfactory performance.

Areas to watch are listed as structural angles, sharp edges, rivet heads, welded joints, particularly when skip welded, or where there is excessive spatter.

Emphasis is also laid on the need for removing all traces of scale and rust before coating, particularly when re-coating old structures.

BARREL PLATING COSTS

The Case for a Realistic Approach

by E. A. OLLARD ★

IN ANY commercial undertaking it is essential that the cost of carrying out the processes concerned should be kept as low as possible, consistent with satisfactory quality. It is also essential that such costs should be known to a reasonable degree of accuracy.

A good deal has been said about works costs and the method of assessing them. It is, however, by no means easy to define exactly what is meant by the "works cost" of an article, and when an attempt is made to define what is meant by the cost of producing a certain article in a factory, it is by no means so easy to put this into words. It is possible to assess the cost of running the factory over a period because this cost is money which is actually paid out by the firm and the costs can be collected from the firm's books and totalled. If the factory is making one article and one article only, it is then possible to divide the sum of money concerned by the number of articles manufactured over the period in question, thereby obtaining the average cost of manufacturing the article. In practice, however, this condition is rarely, if ever, realized. The average factory manufactures a number of articles together, and when dealing with a plating shop, this position usually becomes more complicated, because nothing is actually being manufactured; *i.e.*, articles submitted by the customers are only being finished and these articles are usually of a very heterogeneous nature.

Ideally, it might be considered that the works cost of finishing one of these articles would be the cost of running the factory or shop for a period of, say, one to three months, less the cost of running the factory for the same period doing exactly the same work, except that one of the articles under consideration was omitted. In practice, of course, no difference could be found and such a definition would immediately break down. It is suggested, therefore, that the works cost should be defined as "that proportion of the total running cost of the works which may be arbitrarily assigned to the article in question".

The author is aware that many cost accountants will object strongly to this definition and say that there is nothing arbitrary about the works cost and that it is, in fact, an absolute figure. The objection will be substantiated by means of books and figures, etc., and it will be pointed out that the works costs of many of the products has been worked out to three places of decimals of a penny. The author, however, challenges the cost accountant to define "works costs" and so far no satisfactory definition has been given. It is suggested, therefore, that the works cost is not an absolute figure but depends on the method by which the organization in question decides to break up its total cost figure over the articles it is producing.

However this is done it is essential that the method employed should give reasonable figures which do show, in effect, whether each particular process employed is making a profit or a loss. A costing system is intended to be a guide to help those who control the business to do two things, (a) reduce the cost of the operations to a minimum, and (b) fix a selling price which will yield a reasonable profit margin. Too often it is found that costings systems, if present at all, do not achieve this end.

Factors Affecting Costs

It is usual to divide the cost of producing an article into three main categories, (1) the cost of the labour involved, (2) the cost of the materials used, and (3) the overhead charge covering all costs which cannot be allocated against a particular article, for example, supervision and office charges, maintenance of plant, packing and transport, etc. In some cases this procedure may be varied somewhat as, for example, in many plating shops where such metals as zinc, copper, nickel, etc., are being plated, the cost of the metal involved is small enough to be considered as an overhead.

In most factories the overhead charge is assessed on the labour charges, that is to say, total overheads for a period are divided by the total labour charges for the same period and a percentage obtained which is then added to the average man-hour rate. Thus, if for a period of six months the overhead charge on the shop is £12,000 and the labour £4,000,

* *Atlas Plating Works Ltd.*

the overhead will be three times the labour, or 300 per cent. If a man earning 5s. an hour works for two hours on an operation, the cost of that operation will be 10s. plus 30s., *i.e.*, £2.

In the average plating shop a number of different processes is being carried out and one often finds that these are not costed separately. Usually the manager of a shop is aware whether the shop is making a profit or a loss, particularly if he is an out-plater, when the profit or loss will represent the profit or loss of the company concerned. It is often found, however, that he is not aware of which processes are making a profit and is inclined to consider that they are all functioning equally well and contributing to the total profit of the shop when, in fact, this may not be so. It is therefore advisable for any plating shop to be split up into a number of sections, each of which is costed separately; for example, one section might deal with zinc and cadmium, one with nickel and chromium, one with precious metals and one with barrelling. In such a case the total labour costs are divided among the sections in proportion to the time the men work on each and, as far as possible, the materials costs are also divided. The overhead charge may then be assessed for the shop and split up between the sections on some equitable basis. These are then added to the other charges and subtracted from the money earned by each section as obtained from the invoices, giving the profit or loss.

The principal factors affecting the costs are: the amount of labour required, that is to say, the time a man has spent on the operation and his wage rate; the amount of materials used, for example, anodes, plating salts, etc.; and the amount of time that the necessary apparatus is tied up. This latter factor is included in the overhead charge.

On a barrelling operation, for example, it is obvious that if a man who is getting 5s. per hour can carry out an operation which normally takes, say, 30 min., in 20 min., due to some rearrangement of plant or process, then, other circumstances being equal, the cost of the operation will be materially reduced. It must be remembered, however, that if, in order to obtain this result, it is necessary to tie up some of the plant for a longer period than before, for example, if it is necessary to leave the articles in the barrel for an extra half hour, then it is doubtful whether any real advantage will be gained, in fact it might ultimately prove to be more costly. If work is to be undertaken at the lowest possible cost, all these factors must be taken into account.

The Barrelling Process

Where a number of small articles have to be plated in bulk, it is usual, if possible, to deal with these in a plating barrel. In order to do this the following stages in the process are required and the cost of carrying out each operation must be considered:

(1) Collect articles from customer;
(2) Receive into works, make out works ticket and place ready for process;
(3) Clean and swill;
(4) Acid dip and swill;
(5) In certain cases preliminary burnishing operation;
(6) Plate;
(7) Swill and dry;
(8) Return to customer's container;
(9) Book out and load on lorry;
(10) Return to customer.

In certain cases some of these operations may be omitted; for example, the customer may deliver and collect from the works. However, when all these operations are required, the costs of all of them must be taken into account, although some will, of course, appear on the overhead charge rather than as a direct charge on labour and material. Frequently many of these costs are neglected and the prices quoted are based solely on the time of the operator dealing with the job forgetting the fact that it has to be packed and transported, etc.

Collection of Cost Data

If it is required to assess costs accurately, it is necessary to collect a certain amount of data. In some shops operators are required to punch time cards when they go from one operation to another, but in a plating shop of average size such practices are objectionable as they generally result in lower outputs. The amount paid to each man is known accurately from the wage sheet and also such additional costs as his insurance, etc., so that it is possible at the end of a period, say a month, to obtain the cost to the firm of each individual employed. The cost of materials purchased during that period is also known from the purchase day book. It is, of course, possible that all these materials will not be used during the period in question, while some of the materials that are used may have been purchased in a previous one. However, over a period of, say, six months to a year these small differences are evened out and it is usually sufficient to take the materials purchased and not the materials used, although in a large organization where a storekeeper is employed, the materials drawn from store can be taken as described instead of those actually purchased.

The other costs can be obtained from the firm's private ledger and/or day books and these can be again taken over a period of six months or a year, in which case they should average fairly well. For example, the cost of current, gas, water, etc., can be taken over a period and added together and then

divided by the period concerned, so that an average cost per month, week or day can be found. As stated above, a works cost cannot be considered as an absolute figure, but only an arbitrary proportion of the total costs and it is therefore not worth trying to assess these figures to a very high degree of accuracy. The important thing is that they should show whether an operation is making a profit or loss, and also that they should vary in a reasonable way when articles are required to be more heavily plated or to have special preparatory processes.

Cost of Barrel Plating

In the case of articles plated in a barrel, the cost can be assessed in one of several ways. One's barrel section may be run, for example, for a period of, say, six months or a year and all the costs in this section assessed as accurately as possible, taking the actual labour employed on it, the materials purchased for its use and a proportion of the total overheads of the shop based on the amount of labour employed. At the end of the period the cost of running the section can be subtracted from the amount of money earned and the profit (or loss!) found. This profit can be taken as a percentage of the earnings of the section and if this percentage$=x$, then the cost may be taken to be:

$$\frac{100-x}{100} \times \text{price charged for the article.}$$

Another way, however, is to work out the cost of treating a barrel load. The time involved, the material and the overheads can be worked out and from these a figure obtained to cover the running of an ordinary barrel for, say, one hour. Since the amount of work that can be conveniently loaded into this barrel is known from experience, this amount of work will cost the figure obtained, for every hour during which it is barrelled. Thus, if a load of screws has to be plated with zinc —and it is found that the barrel costs £2 per hour to run—then if the load is to be run for a half-hour, the cost of plating this load will be £1, and if 90 lb. of work is loaded into the barrel this will mean that 90 lb. will cost £1 or 1 lb. about 2½d. If the customer required to have a thicker deposit on his article so that twice the thickness had to be deposited, this would mean that the article had to be barrelled for twice the time and on the above basis this would cost 5d., although in point of fact the cost would probably be less than double since the labour costs of cleaning and preparing the article, together with issue, delivery, etc., would not be increased. On the other hand, if, as often happens, a customer sent the articles to be plated in a number of small boxes and these had to be repacked, the cost of the operation would be materially increased, although the increase would not be shown by the above method.

It is difficult to obtain a costing system which will take care of all these factors. Costing, as mentioned before, is not really an exact science, but is a method of making what one might term, a "controlled guess". However, it should not be despised for this because if careful figures are kept they do give a very good indication of whether the operation is running at a profit or a loss.

It is unfortunate that different firms often assess their costs in different ways, thereby obtaining different results. It is often found that all the methods used can be defended on some score or other, but if, at least, all the out-plating firms can standardize their methods of assessing costs, this would tend to standardize prices charged. Where different methods are used, it will normally be found that one firm places its costs too low for some. types of operation and too high for other types The customer takes advantage of this, giving his order to the firm where he will get the lowest prices and the firms themselves are the losers. Standard methods of costing have been discussed in the trade for some time and some work has been done to try and arrive at these, but at the present moment there is no standard method of assessing the cost of barrel plating and since loads vary very much in themselves, some sort of average has to be struck which for a varied type of article will give a reasonable profit margin.

Cost of Metal Deposited

As previously mentioned, this is usually a fairly small percentage of the whole and is often assessed on an overhead. In the case of cadmium, however, and particularly where work is being plated to specification, the cost of the metal is a considerable proportion of the total and must be allowed for. On 1 lb. of average work, for example, small screws, plated to the A.I.D. specification of 0·0002 in. of cadmium, for every 1 lb. of work plated, two-pennyworth of cadmium is required. Since the total cost of the operation is of the order of 4d. to 5d., this amount of metal will be seen to be a considerable percentage of the whole. If the articles were plated with zinc, the cost would be only of the order of a ½d.; if nickel, of the order of a 1d. Many platers, however, appear to think that the cost of plating with either zinc or cadmium is about the same. For metals such as cadmium and silver, therefore, especially when plated to a specification, it is necessary to take into account the cost of the metal over and above the other charges.

Pricing

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the overhead will be three times the labour, or 300 per cent. If a man earning 5s. an hour works for two hours on an operation, the cost of that operation will be 10s. plus 30s., *i.e.*, £2.

In the average plating shop a number of different processes is being carried out and one often finds that these are not costed separately. Usually the manager of a shop is aware whether the shop is making a profit or a loss, particularly if he is an out-plater, when the profit or loss will represent the profit or loss of the company concerned. It is often found, however, that he is not aware of which processes are making a profit and is inclined to consider that they are all functioning equally well and contributing to the total profit of the shop when, in fact, this may not be so. It is therefore advisable for any plating shop to be split up into a number of sections, each of which is costed separately; for example, one section might deal with zinc and cadmium, one with nickel and chromium, one with precious metals and one with barrelling. In such a case the total labour costs are divided among the sections in proportion to the time the men work on each and, as far as possible, the materials costs are also divided. The overhead charge may then be assessed for the shop and split up between the sections on some equitable basis. These are then added to the other charges and subtracted from the money earned by each section as obtained from the invoices, giving the profit or loss.

The principal factors affecting the costs are: the amount of labour required, that is to say, the time a man has spent on the operation and his wage rate; the amount of materials used, for example, anodes, plating salts, etc.; and the amount of time that the necessary apparatus is tied up. This latter factor is included in the overhead charge.

On a barrelling operation, for example, it is obvious that if a man who is getting 5s. per hour can carry out an operation which normally takes, say, 30 min., in 20 min., due to some rearrangement of plant or process, then, other circumstances being equal, the cost of the operation will be materially reduced. It must be remembered, however, that if, in order to obtain this result, it is necessary to tie up some of the plant for a longer period than before, for example, if it is necessary to leave the articles in the barrel for an extra half hour, then it is doubtful whether any real advantage will be gained, in fact it might ultimately prove to be more costly. If work is to be undertaken at the lowest possible cost, all these factors must be taken into account.

The Barrelling Process

Where a number of small articles have to be plated in bulk, it is usual, if possible, to deal with these in a plating barrel. In order to do this the following stages in the process are required and the cost of carrying out each operation must be considered:

(1) Collect articles from customer;
(2) Receive into works, make out works ticket and place ready for process;
(3) Clean and swill;
(4) Acid dip and swill;
(5) In certain cases preliminary burnishing operation;
(6) Plate;
(7) Swill and dry;
(8) Return to customer's container;
(9) Book out and load on lorry;
(10) Return to customer.

In certain cases some of these operations may be omitted; for example, the customer may deliver and collect from the works. However, when all these operations are required, the costs of all of them must be taken into account, although some will, of course, appear on the overhead charge rather than as a direct charge on labour and material. Frequently many of these costs are neglected and the prices quoted are based solely on the time of the operator dealing with the job forgetting the fact that it has to be packed and transported, etc.

Collection of Cost Data

If it is required to assess costs accurately, it is necessary to collect a certain amount of data. In some shops operators are required to punch time cards when they go from one operation to another, but in a plating shop of average size such practices are objectionable as they generally result in lower outputs. The amount paid to each man is known accurately from the wage sheet and also such additional costs as his insurance, etc., so that it is possible at the end of a period, say a month, to obtain the cost to the firm of each individual employed. The cost of materials purchased during that period is also known from the purchase day book. It is, of course, possible that all these materials will not be used during the period in question, while some of the materials that are used may have been purchased in a previous one. However, over a period of, say, six months to a year these small differences are evened out and it is usually sufficient to take the materials purchased and not the materials used, although in a large organization where a storekeeper is employed, the materials drawn from store can be taken as described instead of those actually purchased.

The other costs can be obtained from the firm's private ledger and/or day books and these can be again taken over a period of six months or a year, in which case they should average fairly well. For example, the cost of current, gas, water, etc., can be taken over a period and added together and then

divided by the period concerned, so that an average cost per month, week or day can be found. As stated above, a works cost cannot be considered as an absolute figure, but only an arbitrary proportion of the total costs and it is therefore not worth trying to assess these figures to a very high degree of accuracy. The important thing is that they should show whether an operation is making a profit or loss, and also that they should vary in a reasonable way when articles are required to be more heavily plated or to have special preparatory processes.

Cost of Barrel Plating

In the case of articles plated in a barrel, the cost can be assessed in one of several ways. One's barrel section may be run, for example, for a period of, say, six months or a year and all the costs in this section assessed as accurately as possible, taking the actual labour employed on it, the materials purchased for its use and a proportion of the total overheads of the shop based on the amount of labour employed. At the end of the period the cost of running the section can be subtracted from the amount of money earned and the profit (or loss!) found. This profit can be taken as a percentage of the earnings of the section and if this percentage$=x$, then the cost may be taken to be:

$$\frac{100-x}{100} \times \text{price charged for the article.}$$

Another way, however, is to work out the cost of treating a barrel load. The time involved, the material and the overheads can be worked out and from these a figure obtained to cover the running of an ordinary barrel for, say, one hour. Since the amount of work that can be conveniently loaded into this barrel is known from experience, this amount of work will cost the figure obtained, for every hour during which it is barrelled. Thus, if a load of screws has to be plated with zinc —and it is found that the barrel costs £2 per hour to run—then if the load is to be run for a half-hour, the cost of plating this load will be £1, and if 90 lb. of work is loaded into the barrel this will mean that 90 lb. will cost £1 or 1 lb. about 2½d. If the customer required to have a thicker deposit on his article so that twice the thickness had to be deposited, this would mean that the article had to be barrelled for twice the time and on the above basis this would cost 5d., although in point of fact the cost would probably be less than double since the labour costs of cleaning and preparing the article, together with issue, delivery, etc., would not be increased. On the other hand, if, as often happens, a customer sent the articles to be plated in a number of small boxes and these had to be repacked, the cost of the operation would be materially increased, although the increase would not be shown by the above method.

It is difficult to obtain a costing system which will take care of all these factors. Costing, as mentioned before, is not really an exact science, but is a method of making what one might term, a "controlled guess". However, it should not be despised for this because if careful figures are kept they do give a very good indication of whether the operation is running at a profit or a loss.

It is unfortunate that different firms often assess their costs in different ways, thereby obtaining different results. It is often found that all the methods used can be defended on some score or other, but if, at least, all the out-plating firms can standardize their methods of assessing costs, this would tend to standardize prices charged. Where different methods are used, it will normally be found that one firm places its costs too low for some. types of operation and too high for other types The customer takes advantage of this, giving his order to the firm where he will get the lowest prices and the firms themselves are the losers. Standard methods of costing have been discussed in the trade for some time and some work has been done to try and arrive at these, but at the present moment there is no standard method of assessing the cost of barrel plating and since loads vary very much in themselves, some sort of average has to be struck which for a varied type of article will give a reasonable profit margin.

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Pricing

Firms quoting prices below an economic level do themselves no good. Although in certain cases, for political reasons, it may be desirable to undertake work for a special customer below an economic

figure, it should never be done through ignorance but only when the firm concerned is aware of the situation and decides to do it for a special purpose.

While it is undoubtedly desirable that a company should endeavour to keep the costs of its operations to a minimum without reducing quality, and while it is admitted that with better manufacturing processes it should be possible to reduce prices to the customer, such prices must not be reduced below a figure which will show a reasonable profit on the operation, otherwise the firm in question is bound to get into trouble sooner or later. The importance, therefore, of accurate costing will be apparent.

Suggested Method of Costing

It is suggested that the barrel section of a plating shop should be separately costed and that if this is large enough to justify it, the costs should be split among various sub-sections of this, that is to say, for example, cadmium, zinc, nickel, chromium, brass, copper, precious metals, etc. The suggested method of doing this has been explained above. If the wages are entered in a suitable book with a column for each section, it is easy to split these up with a fair degree of accuracy and the general shop purchases can be similarly entered and analysed. It then becomes necessary to work out the overhead on the whole shop or business and to decide what portion of this shall be allocated against the barrel shop. This is probably best done by taking the proportion of labour working on a particular section and split the overhead in proportion to this. Thus, if the wages on one section constitute one-sixth of the total productive wages, that is, the wages of all those not charged to an overhead, then one-sixth of the total overhead cost should be allocated against that section.

The amount of figure work entailed is not very great and at the end of a period of several months it is possible to find the total cost of working each section of the shop. Normally it is possible to obtain the price of the work produced from the invoices and it is, therefore, quite easy to see whether the section in question is making a reasonable profit. This information is useful because if the profit margin is satisfactory, it will mean that the pricing of the orders will not be far wrong, although, of course, more profit may be made on some orders than others.

Having worked out the total wages against a particular section and the overhead, then the percentage to be added to the rate of any man working on this section to get the total cost of employing him per hour, can be found. The wage rates vary considerably in different parts of the country, but if a rate of about 4s. 6d. is considered, and it is found that the overhead of the shop is about 300 per cent., then this means that for every hour that the man is employed he is costing the firm 4s. 6d. plus 13s. 6d.=18s.

The average time taken for a man to produce a barrel load of work can be fairly easily discovered by finding out how much work goes through a certain section in a day, how many men are working on it, and how long they work. This can be worked out in the case of a barrel for the weight of the work concerned; thus, a large barrel which holds 100 lb. of work may require, say, a half-hour to prepare, load, unload, swill and dry the work for it. Half an hour will cost, on the above basis, 9s., which would mean that each 1 lb. of work cost approximately 1d. in labour charges. Added to this there would be the charge of the metal, which, in the case of cadmium would be 2d.

This would represent a minimum charge of 3d., to which must be added any additional labour required to sort, or pack the work after plating, and also any additional time taken in such processes as "passivating".

In this way it is possible to work out a price for various loads, it being remembered, of course, that while a barrel may hold 100 lb. of small screws, it may not be possible to put in anything like this weight of odd shaped stampings or wire goods.

If figures are kept over a period, it is comparatively easy to work out the estimated cost for most of the commoner articles which have to be treated. This cost will be checked if profit-and-loss figures are kept for the section in question, and can be adjusted periodically, as required.

In working out a cost, the quantity of material to be treated must be considered; for example, a barrel may take, say, 50 lb. of a certain type of article. If, however, only 40 lb. of this article has to be plated, it will still be necessary to run the barrel in question for the same period of time and the labour costs will be practically the same as if the barrel was completely loaded. If, say, only 20 lb. of work is to be treated, it may be necessary to use a smaller barrel which will probably have a relatively higher labour cost to run, since it often takes just as long to load a small barrel as a big one, particularly in those cases where tackle is provided to deal with heavier loads. Alternatively, it may be necessary to make up a load by mixing two orders and these have to be sorted out afterwards involving considerable extra labour. In every case it must be remembered that when the operator's time is increased it not only means the additional money paid to him but the overhead charge is also to be added.

Particularly on barrelling, the cost can only be kept down when quantities are high and this is a point that should be borne in mind not only by the plater but by his customer.

The cost of the metal used varies nearly directly

with the amount of work plated, and also with the thickness of metal to be applied. This may vary quite considerably under certain circumstances. In some cases the customer requires merely a thin flash of metal to protect the article for a short time, or to give it a satisfactory appearance perhaps to be finally protected by a lacquer. In other cases, a specification deposit may be required, while occasionally, a customer requires an extra heavy deposit, either for some particularly severe conditions or perhaps to increase the actual size of the article so that it may fit into a mating part. When this type of deposit is required, it must be remembered that although the actual work entailed in loading and unloading the barrel may be the same, the time the barrel is occupied with the load will be considerably greater and it usually happens that as a man is detailed to work on a certain number of barrels, if one of these is in use for, say, two or three hours at a time, he may find that he has a certain amount of waiting time which will have to be charged against that order.

Importance of Costing

The importance of obtaining cost figures cannot be too highly emphasized, as previously mentioned, and it is essential that the management of a firm should know, as accurately as possible, what the various processes are costing to carry out, and whether they are making a profit or a loss on the various sections of their works. There is little doubt that if platers paid more attention to this they would, in the end, be considerably better off.

It often happens, however, that prices are quoted without proper cost figures. In some cases prices have been quoted based on the prices other firms have quoted. It is not an unusual state of affairs for the plater when he quotes his price to be told that Messrs. So-and-So have already quoted a price 1d. or 2d. cheaper, and in many cases the plater has then reduced his own quotation on the assumption that if Messrs. So-and-So can do it at that price and make a profit, he can do it at perhaps a lower price still. There have, however, been many cases where the information on which he worked was not correct. Even when he has taken the trouble to verify from the other firm (if he knows them sufficiently well) that the price in question was, in fact, quoted, he may find that this firm also did not base their price on accurate figures.

It is, of course, admitted that prices may vary considerably in different parts of the country owing to labour rates, etc. Usually the rates in London are somewhat higher than those in the Provinces, but these differences are offset by the cost of transport, so that in the majority of cases a London customer does better to have his work treated locally than to send it farther afield. Not only is there the cost of transport, but there is also the time of delivery to be taken into account. Thus, a customer requiring work to be done urgently may be prepared to pay a small premium to make certain that they get it back to a time schedule.

The author would like to urge all plating firms, if they have not already done so, to start collecting cost figures on the basis suggested above. The time involved is only an hour or two a month and this small additional labour is well justified. It is felt that if more firms were truly conscious of the costs involved in undertaking the work that they are doing, there would be less danger of prices being quoted which do not give an adequate return on the work concerned.

It is also hoped that in quoting a price, sufficient margin will be allowed to produce work of a satisfactory quality which should meet the specifications in force and satisfy the customers' requirements. Too often a man quoting a low price in order to get an order, finds that when he has obtained it he has not allowed a sufficient margin to do the work properly and will, therefore, cut the thickness of the deposit or the preparation processes and produce something which, while it may look all right on delivery, will not give satisfaction. This often means that he not only loses further orders himself, but the customer, disgusted with the plated finish, seeks other methods of finishing his goods so that further orders are lost to the whole trade.

Standardization of Prices

Attempts have been made from time to time to obtain agreement on prices for certain types of work Thus, meetings of trade societies have discussed such prices and have advised their members not to reduce their prices below an agreed minimum. If such arrangements could be made and adhered to, there is little doubt that the business would be more profitable. Unfortunately, at the moment there is no trade organization which controls even all the out-plating firms, quite apart from the manufacturers who may have their own plating shops and may from their internal works costs set prices to which they, at least, hope the out-platers will work.

While it would undoubtedly be an advantage to the trade as a whole if minimum prices could be fixed, at least for specification work, the author has very little hopes that this can be done at the present time. However, it is thought that if firms are made more aware of the cost and margin of profit on their work, the tendency to quote an economic price will be enhanced.

Costing by Manufacturers

It has been mentioned above that many manufacturers who undertake their own metal-finishing work put their own works cost of finishing their

(*Continued in page* 36)

A Quarterly Survey of some of the Features in Finishing Literature from Abroad

by **SCRUTATOR**

STEEL sheet and strip which have been zinc coated either electrolytically or by hot dipping are already used on a very large scale in America and are now finding a rapidly increasing market in this country. This is particularly so in the case of the hot-dip material produced by the Sendzimir or Sendzimir-type processes as these zinc coatings are extremely tightly bonded and the coated steel can withstand considerable deformation and bending without rupture or fracture of the protective zinc coating. Under certain storage or transit conditions, however, such galvanized surfaces often form so-called "white rust" or "humid storage stain" and to overcome this a chemical pretreatment is employed. Many of these treatments (phosphate, chromate, etc.) colour stain or etch the metal, thus detracting from the bright, spangled, galvanized surface for which many manufacturers claim a most definite sales appeal. Recent tests by L. J. Brown[1] are, therefore, of considerable interest in presenting a new twin-step approach to this problem of retaining surface brightness and at the same time preventing "white rust" formation. He showed that if the strongly hydrophobic films formed on galvanized surfaces by dipping in dilute aqueous solutions of certain cationic agents were subsequently rinsed in dilute chromic-acid or dichromate solutions, they acquired considerable corrosion resistance while the hydrophobic character remained. The water-repellent compounds tested included fatty amine acetates as well as neutral oleates and stearates but the surface only remained bright with the former.

Another type of staining is that associated with the "*in situ*" cleaning of aluminium surfaces as, for example, in the maintenance of commercial aircraft. This involves frequent washing of the aluminium exterior to remove weather grime, exhaust deposits, etc., using cleaners which in addition to being non-corrosive to aluminium must also be free from the objectionable browning or staining action which many otherwise safe cleaning compounds and solvents display. A method for determining this tendency has been put forward by S. J. Miller and J. K. Stamm[2] using the somewhat unorthodox practice of illustrating photographically the four steps of the technique (with suitable captions) and including no description whatsoever in the body of the article. That at least is one way of overcoming the criticisms which are too frequently justified regarding the English and style of writing in scientific reports !! The illustrations show (*a*) the aluminium test panel and plastic template; (*b*) the template affixed to the panel by an inert adhesive; (*c*) the cavity so formed filled with cleaning compound with solvent and water; and (*d*) the stained area on the panel after removal of the template (and liquid) after 2-hours' test.

Electrodeposition

In many applications, "powder" parts are capable of functioning in the as-sintered condition, but where improved appearance or corrosion and wear resistance are required, some form of electrodeposited coating is often necessary. The results of a comprehensive investigation into the performance of various electroplates on iron powder parts conducted by the Battelle Memorial Institute for the Detroit Arsenal are thus of considerable importance[3]. Baths were investigated for the electrodeposition of cadmium, zinc, nickel, chromium and copper and the more important conclusions were that (*a*) high-density and resin-impregnated parts had a superior corrosion resistance after plating than low-density parts; (*b*) better copper deposits were produced from an acid sulphate than a cyanide bath; and (*c*) nickel-sulphamate and zinc-sulphate baths produced the most satisfactory nickel and zinc coatings respectively.

The requirements of Atomic Energy projects have focused attention on the "rarer metals" and it is perhaps not surprising therefore that among the many characteristics investigated, that of their electrodeposition should have attracted some notice. C. L. Faust and J. G. Beal[4] have reviewed the literature covering methods of plating *on* such metals as beryllium, zirconium, niobium, molybdenum and bismuth and from, as it were, the opposite point of view, M. L. Holt[5] has summarized the literature on the electrodeposition of some of the less common transition metals and their alloys from aqueous solution. Discussion is limited to the metals of Periodic Table Groups IVb, Vb, VIb and VIIIb and a bibliography of 35 references is included.

(*Continued in page* 38)

The Effect of Some Mill Additions on the ABRASION RESISTANCE of a Titania-opacified Enamel

by R. H. ASHBY, B.Sc. Tech. and B. K. NIKLEWSKI, D.Sc. Tech, M.Ph., M.S.

A Paper presented to the Annual Conference of the Institute of Vitreous Enamellers, Brighton, October, 1956

Introduction

ABRASION resistance is one of the most valuable properties of the enamel finish. Some parts of home appliances are exposed to considerable abrasion, so the choice of the right enamel, of the highest possible resistance to abrasion, is of great importance.

Of the many methods used to evaluate abrasion resistance,[1] two have been developed and are used by the industry, in both Europe and America. The Standard Abrasion Test, developed by the National Bureau of Standards has been adopted by the Porcelain Enamel Institute[2]. In this test a sample plate is agitated in a horizontal plane by eccentric motion. Abrasive action is provided by a specified weight of standard felspar and 5/32 in. stainless-steel balls and 5 c.c. of water. The degree of abrasion is measured by the loss of gloss.

The Taber Abraser,[3] is a commercially designed and constructed instrument (Fig. 1). The operation of the Taber Abraser consists of two weighted arms, which press two abrasive wheels against the surface of the sample. The wheels are attached to the weighted arms through ball-bearings, which allow the wheels to rotate, thus equalizing the wear around the circumference of the wheels. The sample under test is clamped centrally to the turn-table which is rotated by a motor at approximately 60 r.p.m. This rotation of the plate causes the surface of the two wheels to rub against the specimen in opposite directions, causing a scratch pattern in the form of crosses, in a circular path approximately half an inch wide. The wheels used for vitreous enamel testing are C.S.17 Calibrase wheels. These are rubber-set carborundum grit, of a coarse grade. A nozzle is provided for attachment to a vacuum cleaner to remove debris from the abraded surface. This is to reduce the rate at which the wheel surfaces become clogged with enamel fragments and to make sure that fresh surfaces are exposed to the abrading action of the wheels. The degree of abrasion is quoted as weight lost after a specified number of wear cycles.

Fig. 1—The Taber Abraser

Both these methods have practical limitations, particularly in the U.K., since for the P.E.I. test, a standard grade of felspar and glass plates for standardizing the instrument are required, as supplied by the National Bureau of Standards, and for the Taber Abraser, special wheels are required which are manufactured only by the Taber Instrument Corporation, and have a short working life.

In this investigation, using the Taber Abraser, the effect of variations in the mill-addition have been studied, since very little has been published on this side of enamel usage. Some work has been published on abrasion resistance of various enamels, by Peterson[3].

Procedure

Preparation of Samples

16-gauge enamelling iron was used throughout the investigation to prevent any possibility of the plates becoming warped during firing. The test plates were cut into 4-in. squares and pierced with two holes, one centrally for clamping to the turn-table, the other in a corner to facilitate weighing. After normal ground-coat application, a sample plate was sprayed with each enamel slip to a wet weight of 4 gm., approximately 35 gm. per sq. ft.

After drying, all the samples were fired at 780° C for four minutes in a small electric muffle furnace. This time-temperature schedule was decided upon after initial temperature and time trials to give the best surface with the basic mill-addition.

Abrasion process

Using a commercial titania-opacified frit with the basic mill-addition, trial runs were made to determine the best procedure for the tests. Curves 3 and 4 in Fig. 4 show the weight losses of two plates abraded for 6,000 cycles with a wheel reface operation of 25 cycles on carborundum paper after each 2,000 wear cycles. The degree of reproducibility was shown to be good. A further test, designed to show whether the tests could be carried out without refacing the abrading wheels, gave the results indicated by curve 5 in Fig. 4. After 6,000 wear cycles, weight losses were negligible, some weighings showing an apparent increase in weight The procedure then adopted was as below:

The sample under test was wiped with alcohol to remove any grease and dirt, weighed and abraded for 1,000 wear cycles. After again wiping with alcohol, the loss in weight was noted and the sample again abraded for 1,000 wear cycles, and the loss in weight noted. The abrading wheels were then refaced for 25 wear cycles and the sequence repeated up to 10,000 wear cycles.

Investigation

The enamel chosen for the investigation was taken from a paper published in the Journal of the American Ceramic Society, Vol. 34, 1951, page 291, entitled, "Study of Particle Size of the Opacifying Phase in Titania Enamels" by M. D. Beals, L. R. Blair, W. R. Lasko and R. W. Foraker. This frit had the percentage composition:

SiO_2	...	41·10
TiO_2	...	20·25
B_2O_3	...	16·91
Na_2O	...	9·31
K_2O	...	7·25
F_2	...	5·18

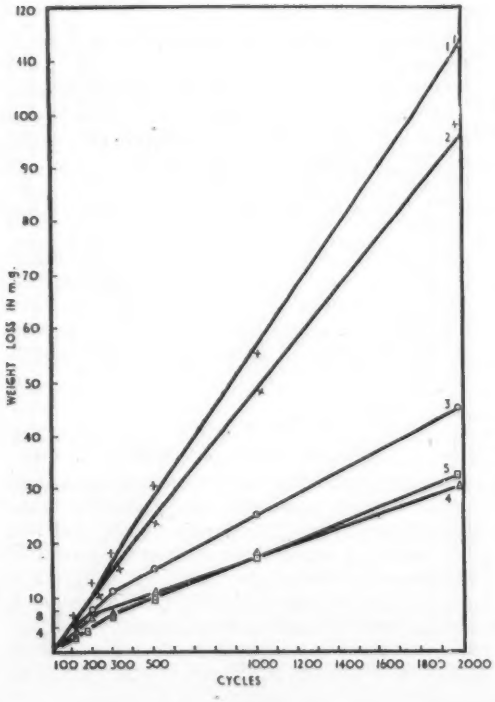
The mill-addition chosen as a base, including the most common materials used for controlling the set of the enamel slip, had the following formula:

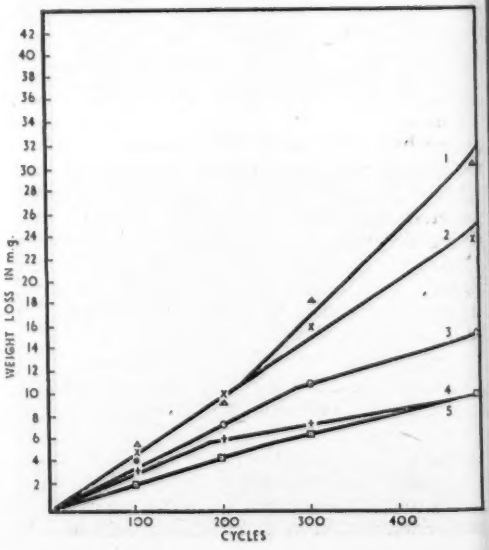
Frit	...	...	100
Clay	...	...	4
Sodium nitrite	...	...	0·25
Urea	...	...	0·25
Potassium carbonate	...		0·25
Sodium aluminate	...		0·25
Water	...	...	42·5

After grinding was complete, further water was added, if necessary, to obtain a suitable sieving and spraying viscosity.

Results

Figs. 2 and 3 show the results, in the form of weight lost by abrasion, of a series of tests carried





Figs. 2 (left) and 3 (below)—Results of abrasion tests. Curve 1. Pre-1940 sample, cut from enamelled plate. Curves 2-5. Commercial titania-opacified enamels.

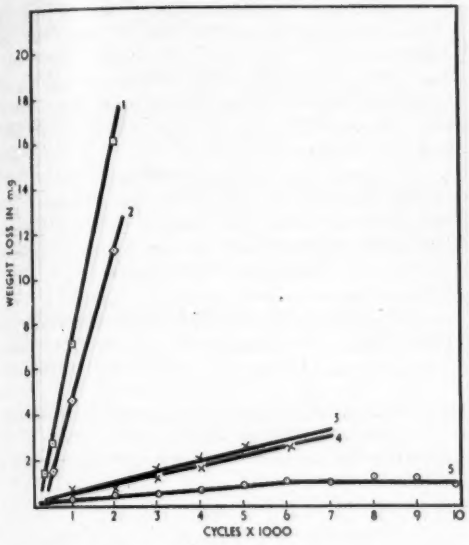


Fig. 4.—Results of abrasion tests:
Curve 1. Acid-resistant antimony-opacified enamel.
Curve 2. Non-acid-resistant antimony-opacified enamel.
Curve 3 and 4. Commercial titania-opacified enamel. Abrasion wheels refaced every 2,000 wear cycles.
Curve 5. Commercial titania-opacified enamel, as used in 3 and 4 without refacing procedure.

out using the wheels supplied with the instrument. These wheels were of the coarse abrasion type. Fig. 4 shows some results obtained with replacement wheels. A comparison of the two figures indicates the considerable difference between the two types of wheels. As wheels of the type used originally were unobtainable, the number of wear cycles had to be increased considerably, from 2,000 to 10,000 cycles.

Figs. 2 and 3 show, a typical pre-1939 enamel compared with a range of titania-opacified enamels. This illustrates very well that though these white cover-coat enamels are possible in only a relatively small composition range there is a great variation in abrasion resistance. There is, therefore, a great deal that may be done in investigating the effect of most oxides on the abrasion resistance of enamels, in a similar way to work already carried out with reference to coefficient of thermal expansion, surface tension, density, and so on.

Fig. 4 shows the low abrasion resistance of two antimony-opacified enamels compared with a titania-opacified enamel, abraded with new wheels, as used in this investigation.

1. *Variation in time of firing, with standard mill-addition.* (*Fig.* 5)

The normal firing time of 4 min. gave a low rate of wear to 1,000 cycles. From 1,000 to 3,000

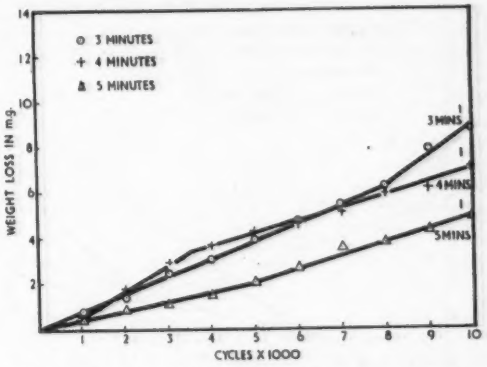


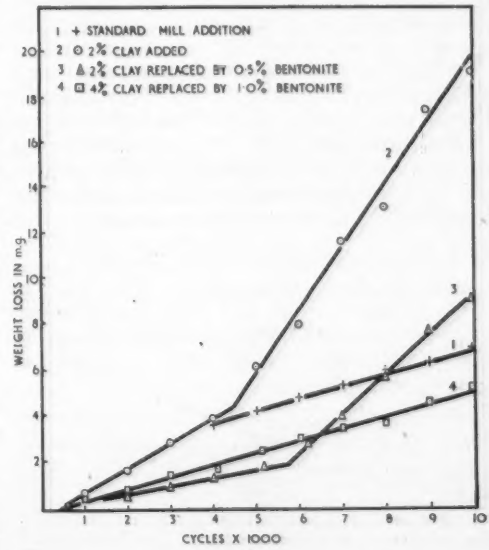
Fig. 5.—Results of abrasion tests on enamels with standard mill-addition but with increasing firing times.

wear cycles the rate increased sharply to 1·1 mg. per 1,000 cycles. From 4,000 to 10,000 wear cycles, the rate of wear dropped to 0·57 mg. per 1,000 cycles. With a firing time of 3 min. the rate of wear was constant at 0·80 mg. per 1,000 cycles to 8,000 cycles, then increased to 1·33 mg. per 1,000 cycles. Increasing the firing time to 5 min. reduced the rate of wear up to 4,000 cycles to 0·42 mg. per 1,000 cycles. From 4,000 to 10,000 cycles, the rate of wear was equal to that for a firing time of 4 min.

2. *Variation of Clay content.* (*Fig.* 6)

An increase of clay from 4 to 6 per cent. made no difference to the rate of wear from 1 to 4,000

Fig. 6.—Results of abrasion tests on enamels with varying clay contents.


1 + STANDARD MILL ADDITION
2 ⊙ 2% CLAY ADDED
3 △ 2% CLAY REPLACED BY 0·5% BENTONITE
4 □ 4% CLAY REPLACED BY 1·0% BENTONITE
WEIGHT LOSS IN mg
CYCLES X 1000

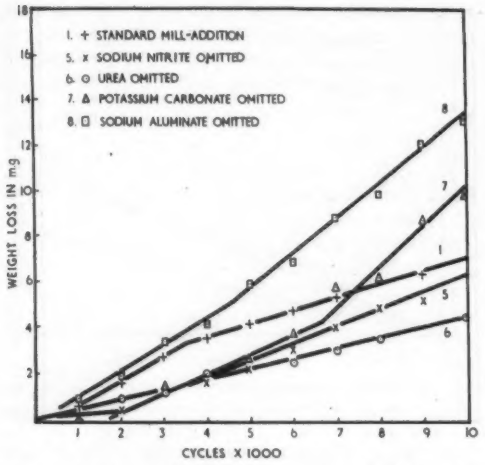

1. + STANDARD MILL-ADDITION
5. x SODIUM NITRITE OMITTED
6. ○ UREA OMITTED
7. △ POTASSIUM CARBONATE OMITTED
8. □ SODIUM ALUMINATE OMITTED
WEIGHT LOSS IN mg
CYCLES X 1000

Fig. 7.—Results of abrasion tests on enamels with varying electrolyte contents.

cycles. From 4,000 to 10,000 cycles the rate of wear increased tremendously, from 0·57 mg. per 1,000 cycles to 2·72 mg. per 1,000 cycles.

Replacing 2 per cent. clay by 0·5 per cent. Bentonite caused a reduction in rate of wear up to 5,000 cycles of 0·22 mg. per 1,000 cycles, to 0·35 mg. per 1,000 cycles. From 5,000 to 10,000 cycles the rate of wear again increased sharply to 1·77 mg. per 1,000 cycles.

Further replacement of 2 per cent. clay by 0.5 per cent. Bentonite apparently reversed the above changes, as the rate of wear for the first 5,000 cycles rose to 0·53 mg. per 1,000 cycles, while the rate of wear for 5,000 to 10,000 range was reduced slightly from 0·57 to 0·53 mg. per 1,000 cycles.

The figures for Bentonite-containing slips were obtained from samples that were badly blistered. Several attempts were made to obtain blister-free surfaces, without success. A change of firing schedule would have resulted in better surfaces, but this would have complicated the reading of the results beyond the object of the investigation.

3. *Reduction in electrolyte content.* (*Fig.* 7)

(*a*) *Omission of sodium nitrite*

This change resulted in a reduction of rate of wear to 0·22 mg. per 1,000 cycles up to 2,000 cycles. Thence to 10,000 cycles, rate of wear increased to 0·74 mg. per 1,000 cycles.

(*b*) *Omission of urea*

The absence of urea decreased the rate of wear to a uniform 0·45 mg. per 1,000 cycles for the whole range. This is, a reduction of 0·7 mg. per 1,000 cycles up to 3,000 cycles, thence a slight reduction from 0·57 mg. per 1,000 cycles up to 10,000 cycles.

(*c*) *Omission of potassium carbonate*

This change reduced the rate of wear up to 2,000 cycles by 1·0 mg. per 1,000 cycles. However, from 2,000 to 6,000 cycles, there was a sharp increase in rate of wear to 0·85 mg. per 1,000 cycles, followed by a further increase, up to 10,000 cycles, to 1·8 mg. per 1,000 cycles.

(*d*) *Omission of sodium aluminate*

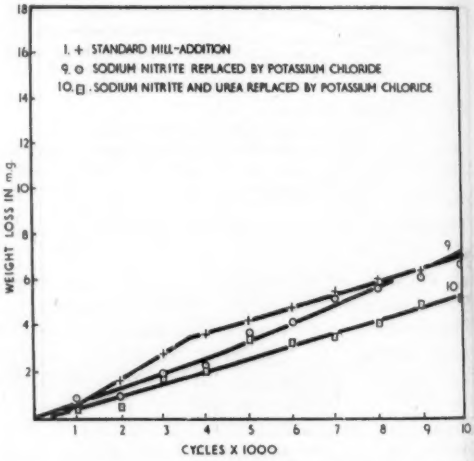
From 0 to 4,000 cycles, this change showed very little difference from the standard mill-addition. From 4,000 cycles the rate of wear increased nearly threefold, to 1·54 mg. per 1,000 cycles.

4. *Partial replacement of electrolytes.* (*Fig.* 8)

(*a*) *Sodium nitrite replaced by potassium chloride*

This change of mill-addition gave reduced rates of wear up to 4,000 cycles, at 0·63 mg. per 1,000

Fig. 8.—Results of abrasion tests on enamels with replacement of certain electrolytes.


1. + STANDARD MILL-ADDITION
9. ○ SODIUM NITRITE REPLACED BY POTASSIUM CHLORIDE
10. □ SODIUM NITRITE AND UREA REPLACED BY POTASSIUM CHLORIDE
WEIGHT LOSS IN mg
CYCLES X 1000

cycles. From 4,000 to 10,000 cycles the rate of wear increased to 0·77 mg. per 1,000 cycles, an increase of 0·2 mg. per 1,000 cycles.

(*b*) *Replacing sodium nitrite and urea by potassium chloride*

This resulted in an overall reduction to 0·55 mg. per 1,000 cycles, in rate of wear. This was a great improvement from 0 to 4,000 cycles, but only a slight improvement from 4,000 to 10,000 cycles.

5. *Addition of Zinc Oxide to the mill.* (*Fig.* 8)

(*a*) 0·5 *per cent. addition.* This addition gave very similar results to those of 4(*b*), the rate of wear being constant from 0 to 10,000 cycles, at 0·50 mg. per 1,000 cycles.

(*b*) 1·0 *per cent. addition.* The amount of wear up to 1,000 cycles was very small. From 1 to 3,000 cycles the rate of wear increased to 0·87 mg. per 1,000 cycles, still below that of the standard and then from 3,000 to 10,000 cycles decreased again

to 0·54 mg. per 1,000 cycles, slightly better than the standard mill-addition.

6. *Addition of ground quartz.* (*Fig.* 10)

(*a*) 5 *per cent. addition.* The rate of wear from 0 to 2,000 cycles was reduced to 0·42 mg. per 1,000 cycles, and increased to 0·87 mg. per 1,000 cycles up to 10,000 cycles.

(*b*) 10 *per cent. addition.* The rate of wear was reduced to 0·42 mg. per 1,000 cycles up to 4,000 cycles. From 4,000 to 10,000 cycles, the rate of wear increased to 0·65 mg. per 1,000 cycles.

Discussion of Results and Conclusions.

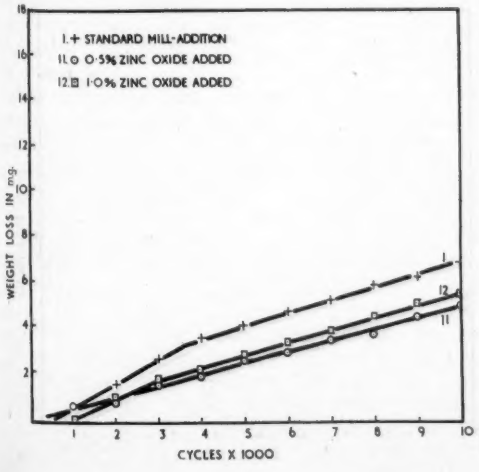
The surface resistance to abrasion or scratching may be increased by:

1. Increasing the time of firing.
2. Reducing or omitting sodium nitrite and potassium carbonate from the mill formula and replacing one or other by potassium chloride.
3. Additions of zinc oxide or quartz to the mill. The addition of quartz should be carefully considered, since the surface appearance deteriorates badly, and an increase in furnace temperature may be required to counteract this deterioration.

To increase the resistance of the subsurface of the enamel to further grinding or abrasion is not really necessary for normal usage of an enamelled product, as deterioration of this severity usually results in replacement of the article. However, the best methods appear to be:

1. Reduction of clay content.
2. Reduction of urea and sodium nitrite. The retention of sodium aluminate appears beneficial to subsurface resistance.

Fig. 9.—*Results of abrasion tests on enamels with additions of zinc oxide.*



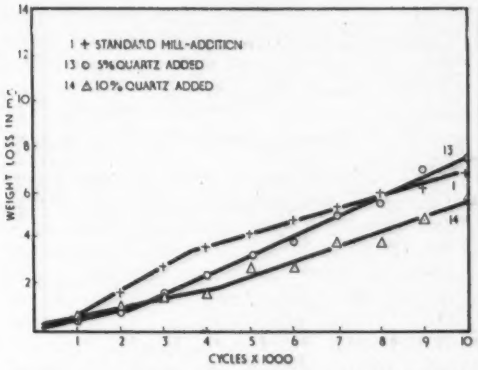


Fig. 10.—*Results of abrasion tests on enamels with additions of quartz.*

3. Addition of potassium chloride in place of urea and sodium nitrite.
4. Addition of zinc oxide.

The abrasion resistance of an enamel as measured by the loss in weight of a sample tested on the Taber Abraser is the resultant of two properties, the resistance of the surface to scratching, and the bond strength of the subsurface.

The resistance of the surface to scratches is dependent on the hardness of the surface relative to the scratching medium and hence on the hardness of the enamel itself. The behaviour of the enamel after scratching is also important in relation to its resistance to abrasion. Some enamels, particularly in the range of titania-opacified enamels, chip extensively from the edges of scratches, even though the scratch does not penetrate the surface layer. This chipping phenomenon is important in that it exposes the weaker subsurface to the abrading action more quickly than in the case of enamels that do not chip in the same way. It has been found in other trials that a 15 per cent. addition to the mill of zirconia prevented this chipping in an enamel scratched by a diamond point.

The bond strength of the subsurface is controllod by the porosity or bubble structure of the enamel, which is dependant on different mill-added materials such as clays, gums, etc., and materials that produce relatively large volumes of gas on decomposition, such as urea.

A further factor affecting the relative thicknesses of the fused surface layer and the porous subsurface is the time-temperature schedule employed in firing the enamelled plate. For the purpose of increasing abrasion resistance a longer time at lower temperature is preferable to a short time at higher temperature, since the latter will result in only a very thin fused skin above the porous subsurface that is easily broken down.

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Discussion

Dr. B. K. NIKLEWSKI, in presenting the paper, said that the vitreous-enamel finish was differentiated from the other finishes paint, some of the plastics, and so, on, mainly by its abrasion resistance. This was the most valuable characteristic of the vitreous-enamel finish, but unfortunately it was taken for granted and, in research programmes, much neglected, probably because the vitreous-enamel finish on most of the panels etc. which were used in daily life was good enough, and much better than any other finish would be. There were, however, some panels used on appliances which required high abrasion resistance, such as the hobs on cookers and the tops of refrigerators, which after several years of use often became badly scratched and abraded. They were, of course, much better than they would be had any competitive finish been used, but some improvement in the case of these special panels was required. There was also the vitreous-enamel finish on chutes for coal and iron ore, where the abrasion was very severe. For this purpose the colour and beauty of finish of the enamel did not matter, but very high abrasion resistance was required.

Whatever might be known on how to provide that abrasion resistance, very little had been published, and very little research work had been done. There was no method by which they could test the abrasion resistance of the finish and compare it with that of other enamel or of the same enamel applied by different firms. The British Standard gave only a Mohs scale, which was a very crude tool for testing abrasion and only served to distinguish enamel from paint; it could not be used to distinguish one enamel from another. An effort had been made to establish a diamond scratch test, and this had given some results, but they could not be repeated when using another diamond, because the edge of the diamond varied and that led to different results.

In trying to do some research on the subject, therefore, the authors had first tried to find a suitable apparatus. On looking at the American literature, they found that the Porcelian Enamel Institute had accepted a method developed by the National Bureau of Standards which was simple and which could be repeated with good results. This was described in the Introduction to the paper. It required, however, the use of a standard and constant grade of felspar, because if the abrading powder was changed the results could not be repeated. The Americans had solved this problem by stocking a large quantity of this standard felspar at the National Bureau of Standards from which samples were obtained when required. The authors had found that if an apparatus of that kind was to be used in this country, it would be necessary to have a standard abrading medium.

There was also another apparatus, the Taber Abraser, which had been developed commercially by the Taber Instrument Company in New York State. This too was described in the Introduction to the paper. They had bought this apparatus, which cost about $450, and all their research work had been done with its help. It used standard abrasive wheels made of rubber with embedded carborundum grit, and the life of the wheel was guaranteed for only one year. For replacements it was necessary to write to the firm, who would send a new wheel which they guaranteed would be exactly the same as the previous one, so that the results from year to year would be comparable. If in this country an effort were made to improve the British Standard method, it would be necessary to have some standard powder or wheel which could be guaranteed to remain the same from year to year. In the course of their work the authors had had to write to New York for new wheels, because the rubber was rather soft and wore quickly. They found that deliveries took about two months.

When they received the apparatus, their first aim had been to find out whether or not their present-day enamels were better than those made before the war, and how to compare one type with another. For example, are the titania-opacified enamels better than the old antimony enamels? The answer was given in Fig. 2, where curve 1 was a pre-war sample, cut from enamelled plate from part of a pre-war appliance, while curves 2-5 were commercial titania-opacified enamels. Fig. 2 also showed something else, which was very characteristic, namely the great differences between the titanium frits; some were nearly the same as the pre-war antimony enamels, while some were much better, in spite of the fact that the composition of the titanium enamels was very much the same, because the titanium precipitated in a very narrow range of composition. Some had a smaller amount of alumina than others, some had some zinc and some had nothing. The range of the possible enamels was very narrow, but among them were tremendous differences in abrasion resistance. There was a Swedish cooker manufacturer, who had

a Taber Abraser and who demanded very highly scratch-resistant enamels, abrasion resistance being one of the criteria for acceptance or rejection. These big differences meant that anyone who made a study of the influence of the composition of the frit would find that some small oxide addition or variation might have a great effect on the scratch resistance. Work on that subject had been completely neglected, so that very little was known about it, but it ought to be done.

The Taber Abraser was illustrated in Fig. 1 of the paper and described, together with the method of operation, in the text. For refacing the abrading wheels, the procedure adopted was to put carborundum paper on the turntable and turn it for 25 rotations, which took off the old surface and produced a new one. They had done some trials without refacing and found that the abrasion was greatly diminished.

The rate of abrasion followed a straight line, being progressive in a completely linear manner. Usually this line had one kink, which occurred at the moment when the surface was destroyed and the abrasion of the sub-surface of the enamel itself took place. If the sub-surface was softer the slope of the curve became steeper; if harder, the curve became a little flatter; but all the abrasion was on a straight line.

They had to consider whether they should deal with the influence of the composition of the enamel on abrasion resistance. They were doing the work with a view to presenting a paper, and they decided to see first of all how mill additions would influence abrasion, because they felt that that would be of interest to the largest group of enamellers. Somebody must prepare an enamel which would be strongly resistant to abrasion, for use on parts of cookers or on coal or ore chutes and so on. The first problem was to find a frit of great abrasion resistance and the second (and this was the aim of the paper) was to find what mill addition to use. Were they all just the same, whatever amount of clay or bentonite was used, or were some harmful and some beneficial?

Dr. Niklewski then went on to say that the authors did not yet know how their measurements related to actual use in practice. They would have to produce enamel which, according to their measurements, would have very good scratch resistance and then use it on a number of components in the field, after a few years getting some of them back and assessing what had happened. It had been stated in an American paper that the measurements made by the Taber apparatus or by the American standard test, were in very good agreement with use in the field. He had done a few panels of spillage trays which he had given to friends, calling them back after two years, and so far he was not very satisfied; the results were not as good as he thought that they would be. He had talked to their customer in Sweden who was so very conscious of the need for scratch-resistance, and he had very definitely stated that there was a great difference; choosing an enamel which was highly scratch-resistant, after a year or two the hobs of the electric cookers which he produced were much better. Dr. Niklewski was not yet prepared to say how the authors results tied up with result in the field. The authors hoped that their paper would be found to contain some useful ideas, and that it would make people more conscious of the importance of scratch resistance.

Influence of Fluxes

Following the presentation of the paper a member said that in explaining the effect of mill additions, the authors suggested that the bubble structure was important, and in regard to sodium aluminate, they pointed out that alumina was a very hard material. It struck him that 0·25 per cent. addition of sodium aluminate, representing perhaps 0·2 per cent. addition of alumina, was very small for the actual hardness to have an effect. Looking at some of the things which improved the hardness, he found they were sodium aluminate, potassium chloride and zinc oxide, materials which had in common the property of being fluxes. He wondered whether or not that property was associated with the degree to which the clay added at the mill went into solution in the enamel. An increase in firing time, which was likely to increase the amount of solution of the clay, also improved the hardness.

In addition, there was a difference between the hardness of the surface and the hardness in the bulk of the enamel. It might be expected that the surface might be subjected to more heating and that therefore there would be more solution in the surface. Unfortunately that idea did not tie up with the authors' silica additions, but if they put in 5-10 per cent. the amount would probably be sufficient for the actual hardness of the silica itself to be effective. He was not sure how sodium nitrite came into the picture and whether or not it was a less efficient flux than potassium chloride. Perhaps the authors would have some observations to make on the subject.

Dr. NIKLEWSKI replied that it was difficult to say that a very tiny addition of alumina could have a great influence on hardness. It was true that alumina had a very high coefficient of hardness. As he had said, it was just a supposition. There was only the one explanation which the authors could find, because the question of a flux did not tie up with the results at all. Some enamels which were very difficult to fuse were not hard at all, while some others which were very fusible had

very high scratch resistance. Hardness and resistance to abrasion and scratch, therefore, were not bound up with the fusibility of the enamel. The authors had definitely proved that they were two separate things, and, from some small trials which they had done, he would say that the connexion was even less than with acid resistance. Usually the acid-resistant enamels were more difficult to fuse than the others, but a very soft enamel could have a fairly high scratch resistance, and quite often the titanium enamels which were much harder were not scratch-resistant at all. If it were only a question of flux the problem would be simple, but it was not; there must be something more complicated, such as the question of the atomic size in a glass structure. Probably it would be found that if the diameter of the molecule was large there would not be much scratch resistance, while the glasses with a close bonding would probably have more scratch resistance, but that was only supposition.

It was easy to put forward many theories to account for what happened. The authors made use of those theories for pursuing their research, but only went by the actual measurements. The theories were important in deciding what should be the next step to take. They had found that a small addition, 0·25 per cent., of alumina improved the scratch resistance. After looking at the table, they then decided to try zinc, and it happened to be good, but that had only been guesswork. That was how they carried on research. They knew very little about scratch resistance and did not know the influence of the components on scratch resistance. More work had been done on glass, because glass was used for bearings, and a great deal of research had been carried out to find hard, abrasion-resistant types of glass. They were all based on very high alumina, about 30 per cent. A great deal of research work was involved in trying to find the influence on scratch resistance of various factors. They must expect to find not straight lines but curves, with improvement up to a certain percentage and then deterioration and so on.

Mr. N. S. C. MILLAR (Frit Factory, Radiation Ltd.) congratulated the authors on an excellent paper and referred to their comparison of pre-war with post-war enamels. To test the pre-war enamel, apparently, they cut a piece from enamelled plate and tested it in the Taber Abraser. Presumably on the Abraser a certain amount of heat was evolved, and it was known that the thermal shock resistance of enamel deteriorated somewhat with age. Did the same sort of deterioration occur with scratch resistance? If this pre-war enamel had been put on now, would it have had superior scratch resistance under the test?

There had been no mention at all of the effect of titania in the mill. Would it have had the same effect, for example, as the addition of zirconia? The effect of titania at the mill would be of importance with a saturated enamel rather than a supersaturated one. The authors' comments would be of interest.

Dr. NIKLEWSKI said that the measurement of the pre-war enamel and its comparison with the enamels of today had been done for the benefit of their critics amongst the public, who always said that everything was much better before the war than it was now. The result of that tendency had been a great deal of criticism of post-war enamels, and so they had cut out a piece of pre-war enamelled plate and tested it and found that it was not so good. To the question of whether it had deteriorated with time he could only reply that they did not know. They knew that the resistance to thermal shock deteriorated after ageing for a few weeks, but they had no information so far as deterioration in scratch resistance was concerned and he could not answer the question.

They had done some measurements on the addition of titania, because using titania enamels and trying to produce cooker components, which would satisfy their customers had made them very critical. About two years ago they had tried adding a few per cent. of titania. At that time they did not possess the Taber apparatus and had used the diamond scratch test, and they could not see any benefit by the addition. The Taber apparatus showed a tremendous difference between a good and a bad enamel, and it was possible to repeat the measurements with some exactness. It was a very accurate apparatus. The diamond point test, on the other hand, was crude, and made very little differentiation. What was only a small difference judged by the diamond point test showed up as a big difference with the Taber Abraser. Using the diamond point test two years ago, and adding only a few per cent. of titania, they did not find any benefit. Zinc and quartz made a big difference, and zirconia prevented chipping.

Mr. MILLAR suggested that titania also would prevent chipping.

Mr. R. H. ASHBY said that they had used only up to 3 per cent. titania, and, as Dr. Niklewski had said, the differences had been very slight indeed. They had not pushed the addition up, as they had with zirconia. He thought that the same problem would arise with titania as with zirconia; the surface appearance deteriorated so quickly that it would not be possible to use the large quantities required.

Mr. A. W. MURDOCH (Ferro Enamels Ltd.) said he could appreciate some of the difficulties which the authors had encountered, as he had had something to do with work of the kind in question over a period of time. Dr. Niklewski had already partially answered the question he wished to ask.

They had had an opportunity, over a long period of time, of comparing the results of this type of abrasion and sractching, using equipment which was basically similar to that mentioned in the paper, which had been awarded the Whittle Prize four or five years ago. The results which they had obtained were similar in gradation to those obtained using the P.E.I. tester or the Taber Abraser. With the P.E.I. tester there was a much larger difference of result, but the same result could be obtained using the scratch resistance test.

If any test of the kind in question was to be of importance to the industry, it would have to be something which most enamellers would be able to purchase and use, so that it must be relatively cheap. The Taber Abraser and the P.E.I. equipment might be rather beyond the pockets of most people. In view of the fact that the same gradation of results was obtained and that there was no real difficulty in standardizing control with the cheaper type of equipment, would the authors still prefer to put forward the test which they had been using?

Dr. NIKLEWSKI replied that he could not put forward the test which the authors had used for acceptance in this country. It was very expensive and new wheels had to be obtained periodically from America. It was the tool for research, but not apparatus which he would suggest should be used as a British Standard test. They had a very tough problem ahead of them in deciding how to improve the British Standard test. The Mohs scale was a childish tool; it differentiated between enamel and paint and nothing more. A knife would differentiate betwen enamel and paint simply by scratching it. If they wanted reproducibility of results, and results which would be the same when obtained in different laboratories and by different manufacturers the apparatus would have to be rather elaborate and expensive. Probably the P.E.I. apparatus represented the best value for money. People must be prepared to spend £30 or £40 for the equipment. It would probably be difficult to get anything cheaper. The problem would be discussed in the Technical Committee. His present feeling was that they should not accept the Taber Abraser, but should use apparatus similar to the P.E.I. apparatus. It would then be necessary to stock the standard abrasive material, because only if that were done could good results be obtained. Some place in this country must hold two or three tons of the standard felspar or quartz, or whatever was chosen, and all the material used must come from this stock, because if the abrasive material was changed it would be necessary to start again.

Mr. E. W. B. DUNNING (Gas Council, Watson House) said that users did not want to have to test samples; they wanted to test the big pieces, and that was always a difficult problem. Had the authors any information about the kind of apparatus which the Americans used for this purpose? They were very conscious that the Mohs scale of hardness test was not satisfactory. They had instituted it many years ago, but in all the time which had elapsed since, no one had produced anything which could be applied to existing parts which was better.

It was well-known that when one started looking for scratches there was a tremendous difference between the perception of different people and according to the particular light under which the object was viewed. One of his assistants was an expert at finding scratches on enamel.

On the question of spillage trays, at the end of the war, there had been a shortage of sheet steel and a large number of cookers had been sent out with aluminium grill pans. Aluminium was a very soft metal, and they had been surprised to find that the abrasion of the pans was extremely high, very much more than before. That seemed to be due to the fact that grit from ordinary household cleaning powder became embedded in the soft aluminium, and it was not so much the abrasion of one piece of enamel or aluminium on the enamel which was the cause of the trouble, but rather what there was between the two surfaces, which was the real abrading medium. The more modern method of hanging grill pans, so that one did not get the perret marks underneath, would obviously help there.

Without accurate experimental knowledge, he was afraid that they could not support the contention that enamels today were much better than they used to be. They felt that there had not been much improvement. They had crown trays returned to them which were very heavily scratched.

Dr. NIKLEWSKI, replying to the question of whether there was an apparatus which could be used on components, without having special plates, said that the American P.E.I. tester was very good and could be used for the purpose with a small addition, a guillotine to cut out a piece. It would be extremely difficult to devise an apparatus which would test whole components.

With regard to the pre-war enamel, the authors did not know to what extent their measurements were tied up with the scratching material used, and the results obtained in the field might be different from those obtained in the laboratory. On their own measurements, the titania enamels were better than the antimony enamels, but the difference in scratch resistance in service might be very small.

Mr. DUNNING said that his organization would always be prepared to assist in field tests. If any manufacturer or group of manufacturers had, say, a thousand crown trays which they wanted to test,

his organization would be prepared to buy them and put them on cookers and report the result at the end of 12 months. They were prepared to work with the manufacturers. They had their customers up and down the country. With holloware, nobody knew who the customers were, but the gas industry knew its customers and could go back to them after a period of time and find the equipment still there, so that they could examine it. They were always prepared to do that in order to co-operate in carrying out filed tests. In the end it was only the customer who could be right, and they themselves were not really the customer.

Scratch Resistance and Porosity

A member suggested that it was possible to correlate porosity with permittivity, and that on that basis it might be possible to find a non-destructive test by measuring the permittivity. Some work had been done in America which correlated porosity with the scratch resistance of the material.

Dr. NIKLEWSKI agreed that a paper had been presented in America correlating scratch resistance with the bubble structure and porosity of the enamel. It was the porosity, therefore, which was responsible for the low abrasion resistance. To measure the porosity by using gases or liquids and then assess the scratch resistance would be difficult, but without any structure, which could be used and introduced in the form of gas bubbles, or some crystalline material or some grit or whatever it might be, varied greatly with the composition, and the glass itself varied with the composition of the different idea put forward for research work was a constructive one, and it might be possible to measure the transparency to liquid and find out the scratch resistance, but it was a very complicated problem.

Asked whether any ideas had been formulated during the authors' work on the question of the flexibility of enamel and abrasion resistance as it seemed possible, that increased flexibility of the enamel would give increased abrasion resistance, Dr. Niklewski said that they did not know the answer to that. It might be possible to correlate abrasion resistance with many of the other characteristics of enamel, such as fusibility and acid resistance, but they did not know. They had not been thinking in their work about elasticity or flexibility of the enamel.

Mr. S. E. A. RYDER (Stoves Ltd.), after thanking the authors for their pioneer work, said that Dr. Niklewski had mentioned the different resistance to abrasion of the skin and the body of the enamel. Most enamellers, however, were concerned only with the abrasion resistance of the skin; once the surface cracked the article had deteriorated. Did the authors' instrument differentiate readily between the resistance of the skin and that of the body, and would it be useful to express the results in terms of the number of cycles to remove the first milligram, rather than the other way about?

Dr. NIKLEWSKI recalled that usually the abrasion resistance was a linear function, a straight line. In Fig. 6 some of the curves, and in particular Nos. 2 and 3, had a kink in them. Up to the kink the line represented the resistance of the skin, but then the skin broke down and the line showed the resistance of the body. When the line was straight from beginning to end it meant that the resistance of the skin was equal to the resistance of the body. With high clay the skin was harder, and then the line broke and gave the resistance of the body.

Mr. RYDER asked whether it was possible to lay down a figure of loss at which it could be said that the surface had gone.

Dr. NIKLEWSKI replied that that could be determined from Fig. 6. In the case of curve No. 2, there was a loss of about 4 mg. at 4,500 cycles. In the case of curve No. 3, where the enamel was a little harder, there was a loss of only some 2 mg. at 6,000 cycles. From the form of the curves it was apparent that in the second case the skin was thinner, but could stand more abrasion. Their interpretation of a straight line from beginning to end was that there was no difference between the skin and the body. Where the curve bent downwards at the kink it meant that the skin was softer than the body. Clay enamels had harder skins, and then there was the bubble structure and the line went up.

Asked whether there was any prospect of getting satisfactory abrasion wheels for the test from sources in the U.K., Dr. Niklewski said that the authors' first reaction, on getting the Taber apparatus, had been to look in this country for a supply of rubber rings. They had done some research on the market to see how it could be done, but the rubber presented a difficult problem. It was essential to have a guarantee that the hardness of the rubber would be exactly the same year after year, and they must know how long it would take the rubber to harden. The American firm gave a guarantee for one year and would supply a new pair of wheels, which would give the same measurements as the first, and they guaranteed to do this for some years. They hoped to find a supplier in this country who could do the same, because at present for each pair of wheels an application had to be made to pay the $4, which meant a lot of paper work to get the wheels.

Mr. J. W. PEDDER (Stewart and Gray Ltd.) said that the importance of homogeneity was very great, and he thought that that was generally accepted. Had the authors carried out any experiments on a piece of plate glass, and, as an alternative,

(*Continued in page* 38)

The PRETREATMENT of METAL SURFACES

A Review of Some Proprietary Processes

By MAXWELL LEWIS, M.A., B.Sc., M.S.A.E.*

(A paper presented to the North-West Branch of the Sheet and Strip Metal Users' Technical Association)

IT is necessary to ensure that a metal surface is properly prepared for the following reasons: First, to impart to the surface a property which is not an inherent characteristic of that surface: for example, it might be required to provide a metal surface which has little or no natural affinity for paint (where paint adhesion is naturally poor) with a key for an organic finish.

Second, to enhance or improve a property which is already a characteristic of the metal: for example, to improve upon an existing affinity for paint by providing a key which will resist corrosion, or to improve the resistance to wear of moving parts in contact.

Third, to eliminate or subdue temporarily or permanently, inherent properties which are undesirable, hazardous, or likely to lead to difficulties in fabrication. The simplest example of this is cleaning or degreasing, to remove oil and grease. An example of the subduing of a permanently inherent property is the inhibition of rusting.

Purposes of Metal Preparation

Having briefly surveyed some of the reasons why metal surfaces need preparation it is logical to enquire for what purposes, or with what objects metal surfaces are prepared. Of main importance is the provision of a bond for organic finishing and in most cases one which will preferably also act as a protective against corrosion, and paint failure and flaking from that cause. Other reasons include the inhibition of, and protection against, corrosive attack, the reduction of wear on moving parts, the inhibition or prevention of fretting corrosion, the facilitation of cold-forming operations and the necessity to carry out preparatory treatments as a prelude to metal colouring for decorative purposes and for electrodeposition.

It must be emphasized that the achievement of any one objective is unlikely to be secured by a single operation but on the contrary will demand the carrying out of a train or sequence of operations. The reason for this is that the elimination of one undesirable property may create or establish another which in its turn must be corrected.

If, for example, it is necessary to paint a ferrous surface, thus degreasing alone is not adequate as normally the surface is rusted. Degreasing, therefore, can be followed by shot blasting which removes the corrosion products and further cleans the surface, and also provides a mechanical key for the final finish. After this treatment, however, it will be found that the resulting "activated" surface rusts more rapidly and thus the final finishing treatment should be carried out as soon as possible.

It should be realized that the provision of a coat of paint immediately after shot blasting will prevent the surface rusting for a short time, but good as it may be the mechanical key has no protective or corrosion-resisting properties, and to provide these further operations are necessary.

The precise operations involved in solving any given problem must depend upon the nature and requirements of the problem, the environment or locality, and the materials concerned. The means adopted may be purely mechanical or purely chemical, or a combination of both.

Mechanical preparation is most commonly associated with cleaning, removal of scale, corrosion products, etc., and may involve sand or shot blasting, vapour blasting, wire brushing and in some cases tumbling. There are also the surface improving operations of polishing and buffing—not strictly metal preparatory treatments.

Chemical preparation covers degreasing and pickling, to remove surface impurities such as scale and corrosion products. Pickling and its associated rinsing operations has the effect on ferrous materials of leaving an activated besides a clean surface, like shot blasting, and, in a similar fashion, rusting will quickly occur if no further operations are carried out.

Chemical pretreatment of the surface as distinct from chemical preparation covers a wide range of operations whereby a conversion of the surface takes place with the formation of an integral,

* *The Pyrene Co. Ltd.*

non-metallic coating which may be an oxide, phosphate, oxalate or chromate.

For resisting corrosion and for paint bonding, ferrous materials are commonly pretreated by phosphating.

Two widely used proprietary phosphate processes are "Parkerizing" and "Bonderizing," the former being used in circumstances where maximum resistance to corrosion is required and the production concerned does not need a decorative finish. It is a two-stage system:

First, the parts concerned are given a phosphate coating of relatively high coating weight and afterwards this coating is impregnated by dipping, spraying, tumbling or brushing with the Parker finish appropriate to the application. Some "Parkerizing" specifications, as for example, structural steelwork, Bailey bridges, etc., do call for painting after "Parkerizing."

Coating weight in terms of milligrams per square foot of surface is the nomenclature normally used to describe the thickness or heaviness of phosphate coatings. A Parker coating is normally in the range 1,000 to 4,000 mg. per sq. ft.

"Bonderizing" is the range of phosphate processes which meets the requirements of pretreatment prior to painting or stove enamelling. The coating weight of a "Bonderite" coating is in the range 150 to 500 mg. per sq. ft. dependent upon the process, the material involved and the method of application.

Other phosphate processes in industrial use are those marketed under, for example, the trade names "Walterising" and "Granodising."

For the preparation of aluminium before painting there are acid chromate, and alkali chromate processes, which produce oxide coatings, and there is also a phosphate process for this metal. The acid chromate processes are the "Bonderite '710'" process and the "Alocrom" process. The alkali chromate processes are: "Pylumin" and the M.B.V. process. The phosphate process is "Bonderite '170'."

Zinc can be pretreated for organic finishing by phosphating, or by chromating. Of the last, the oldest and best-known is probably the "Cronak" acid-chromate process which produces a coating of basic chromium chromate. Chromating applications are, however, of principle significance for the protection of zinc-plated parts which are given no further finishing treatment. For preparation prior to organic finishing, phosphate treatments are most commonly employed. Zinc has no affinity for paint. On the contrary, zinc soaps tend to form by reaction with the paint and cause paint peeling.

Cadmium surfaces can also be protected by chromating or they can be phosphated if subsequent organic finishing is called for.

A great deal of attention has been given, particularly in the last few years and in America, to the treatment of magnesium before painting. This no doubt derives from its attractively light weight relative to structural applications despite its active nature. Once again paint adhesion is by nature extremely poor, but further, the chemically basic products of corrosion readily promote underfilm attack. In connexion with aircraft applications, during the war the R.A.E. devised a chromating process, covered by a Ministry DTD specification involving a 30-minute immersion in a hot solution containing potassium dichromate, ammonium sulphate and dichromate and ammonia; the paint bonding properties of the resultant coating are good.

Some six or more processes have been described covering anodizing as well as chromating treatments and the most recent ones, also electrolytic, are described as being electrolytically applied ceramics usually 0·001 in. thick. The coating is akin to a glass, and corrosion, heat, and abrasion resistance are said to be good but the elastic properties are poor and the coatings are very easily cracked.

Ferrous materials are also phosphated to assist lubrication and reduce wear. The process most commonly used is "Parco-Lubrite" in which the absorptive characteristics of the phosphate coating is employed to retain oil; in addition, the crystals are uniform in size thus enabling allowance to be made for working tolerances.

In the wire-drawing and tube-drawing industries modified "Bonderizing" processes are used to facilitate these cold-forming operations. In these applications the phosphate coatings act as parting layers between the work and the die, and hold the lubricants involved.

Another "Bonderizing" process, "Bonderite 'SS'," is used for facilitating the cold working of stainless steels and heat-resistant alloys like Nimonic. In this case, however, the coating is an oxalate coating, not a phosphate.

Importance of Cleaning Procedure

In metal pretreatment practice the first operations invariably carried out are cleaning operations. Too much importance cannot be placed upon them as, generally speaking, the coating it is intended to apply to the metal is only as good as the surface to which it is applied, if indeed it can be applied to that surface at all.

Cleaning must be regarded as a task which is completed in two stages although the second is not always required. The first has as its object the removal of organic substances, like oils and greases (degreasing) and the second, the removal of inorganic substances like scale, rust and corrosion products (descaling).

Alkali Cleaning

The choice of the degreasing method adopted depends upon a variety of factors such as the nature of the contaminant to be removed, the production circumstances, and also the ultimate finishing technique to be used. The most usual method of cleaning is alkali cleaning which is applied by immersion or spray or a combination of both using hot solutions, commonly of proprietary mixtures.

Alkali cleaning is always followed by water rinses which can be hot or cold according to local circumstances and needs. Spraying systems offer the advantage of impact in addition to emulsifying power, which is effective in breaking down obstinate or difficult materials and in removing soil from the surface.

Solvent Cleaning

Solvent cleaning methods are also widely used. Hydrocarbons are probably the best solvents but have the disadvantage of flammability, and chlorinated hydrocarbons are also good solvents but toxic. Nevertheless these two groups provide, almost exclusively, the materials used, and methods of using them vary from hand wiping with white spirit to conveyorized equipment for liquid followed by vapour degreasing with trichlorethylene and similar compounds. It should be noted that solvent vapour degreasing will not remove soaps, water, soluble salts, or soil. Solvent cleaning is also apt to be expensive when compared with other methods.

Emulsion Cleaning

Increasing use has been made over the last decade and principally in spray machines, of emulsion cleaners which consist mainly of kerosene emulsified with water, and sometimes containing small amounts of alkalis. These cleaners are satisfactory when dealing with mineral oils but are not generally so successful with vegetable oils. They are operated at fairly low temperatures in aqueous solutions, and are followed by clean water rinses.

There are also emulsifiable cleaners in which emulsification occurs during subsequent rinsing. Some of these materials can be used at room temperature and are particularly suitable for degreasing large objects in specialized or limited production. Rinsing is then most effectively performed by high-pressure hosing, the impact aiding emulsification.

Diphase Cleaners

A comparatively recent modification of emulsion cleaning practice is the development of diphase cleaners which are particularly effective in some applications. Diphase cleaners cause the metal surface to be subjected to the simultaneous action of emulsion and solvent. Thus, the solvent removes oils and wets the metal while the water takes care of water-soluble materials and wets mineral oils.

Ultrasonic Cleaning

Over the last year or two the use of ultrasonic waves in cleaning has received attention, with notable success in certain applications. Both solvent degreasers and detergents are used, the high-frequency source or "transducer" being immersed therein. The principle involved is the establishment of a high degree of agitation at the surface of the part being degreased thereby improving the operation either in the speed with which the cleaning operation is completed or in the degree of cleanliness attained or in both. Frequencies of the order of 430,000 cycles per second are employed and in America conveyorized ultrasonic equipment is now being supplied.

Descaling Operations

With regard to descaling little need be said except perhaps to emphasize that both mechanical and pickling methods activate the surface. For scale removal inhibited sulphuric or hydrochloric acid pickles are used, and for the removal of rust and corrosion products only, phosphoric-acid-based materials are very frequently employed.

Flame cleaning, which utilizes the differential in coefficients of thermal expansion of metal and scale is sometimes employed on structural steelwork and where large areas are to be descaled. A comparatively recent development in heating techniques is a process for removing mill scale by induction heating which may lend itself to the continuous treatment of strip or rod.

PHOSPHATING PROCESSES

It is said in the literature that there is evidence that some form of rudimentary phosphating technique was practised by the Romans in the third century and that about 1,500 years later it was noted that rusting of the metallic parts of girls' foundation garments was retarded by treating them with phosphoric acid. A variety of compositions (apparently of Alchemic origin) were described from time to time up to 1908 when Coslett developed the first process of any commercial significance. Phosphating became a truly accepted process in 1916 with the development of "Parkerizing" by the Parker Rust Proof Co., of Detroit, U.S.A.

"Parkerizing"

All the early attempts at phosphating had rust-proofing or the retarding of corrosion as their objective. Coatings produced were of the heavy type and took a long time. Phosphate coatings are not in themselves sufficiently protective and need

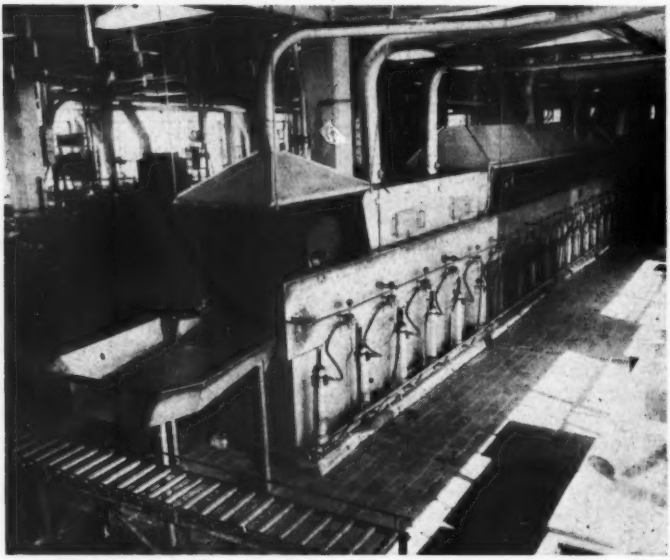


Fig. 1.—Pneumatically-operated tipping-basket type "Parkerizing" plant at Singer Manufacturing Co. Ltd.

to be sealed, but the absorbent nature of the coating provides an excellent base for the impregnating medium used which, originally, was oil or wax. The surfaces so treated retained this material for long periods, the combined system proved powerfully rust resistant, and provided a very useful method of treating such components as nuts and bolts, washers, brackets, castings and sheet-metal pressings, etc., which did not call for a decorative, high-quality finish.

The plant required was of the simplest, *viz.*, mild-steel tanks of appropriate dimensions determined by the size of components to be treated and the volume of production, equipped for steam or gas heating and providing for processing and rinsing, dry-off facilities, and perhaps an additional tank for holding the impregnating medium. Parts were treated in baskets or in rotary barrels for the operating of which processing tanks were suitably equipped.

Equipment of this kind is, of course, still in use today for low- and medium-volume production, but the rapid developments which have taken place over the years in production engineering and their influence upon industrial finishing have demanded that "Parkerizing" keep in step. Accordingly, processing times have been reduced from 60 minutes to 5 minutes, operating temperatures have fallen, and there are now seven "Parkerizing" solutions covering all requirements. A range of special Parker finishes includes finishes for general engineering applications, camera parts and small arms, and rinsing has been modified by the recommended addition in most applications of a rinse in very dilute chromic acid (chromate rinsing).

The needs of high production volumes have been met by tipping-basket type "Parkerizing" machines. When these were first introduced in 1947 they were comparatively small and hand-operated, but now pneumatically-operated plants treat small parts at the rate of thousands of pounds weight per hour, and the latest types of hydraulically-operated electronically-controlled equipment now under construction will increase this so that tons of components can be treated every hour.

"Bonderizing"

With the speeding-up of processing time by the use of accelerators and increasing experience of the zinc-phosphate type of solutions, attention was given to refining the coating and reducing grain-size. Soon a phosphate process was evolved which provided a coating which was eminently suitable

Fig. 2.—Metal-finishing shop at the Quinton Road factory of Armstrong Siddeley Motors Ltd. "Parkerizing" and anodizing processes are included among the facilities available.

Fig. 3.—The "Rotodip" plant at Fisher and Ludlow Ltd.

as a base for paint. This first "Bonderizing" process, introduced in America in 1926, had a processing time of about 10 minutes and was applied by immersion.

Advantages of "Bonderizing"

It is a feature of the process that a surface conversion takes place and the phosphate coating is uniform over the metal surface and integral with it. It is crystalline, non-metallic, highly absorptive, and electrically an insulator. The surface is absolutely clean, free from grease and from corrosion products and in this respect it acts as its own inspector. If after passing through the degreasing sequence there is residual grease on the metal, the greasy part will not process. The same is generally true of corrosion products. Paint adhesion is improved through the absorptive nature of the coating. Next the coating subdues corrosion, and should the organic film be cut through or damaged, rusting is confined to the area of damage and failure of the finish through corrosion creep is either eliminated altogether or very greatly reduced.

"Bonderizing" for Zinc Surfaces

At first only ferrous metals could be processed but a "Bonderite" process was soon developed for treating zinc and zinc-alloy surfaces. This was followed by a solution in which ferrous parts could be "Parkerized" and "Bonderized" dependent upon the immersion time, and ferrous and non-ferrous surfaces treated separately or in mixed production if so desired.

"Spra-Bonderizing"

New accelerators speeded up reaction rates still further and processing times were reduced to 60 seconds or less. This enabled the solution to be applied by spraying and a new range, the "Spra-Bonderizing" processes, became available to industry, thus meeting the requirements of flow-production methods. "Spra-Bonderizing" machines are now designed whereby oily and greasy work is introduced at one end and emerges "Bonderized" and dried ready for the application of the finishing sequence from the other. Cycles, motor cycles, car bodies, refrigerators, fluorescent light fittings, office furniture, are typical examples of products which are prepared for painting in this way.

"Roto-Bonderizing"

The introduction of chassis-less construction by the British motor industry produced new pretreatment problems relative to the treatment of the insides of the box sections which are a feature of this method of fabrication. From the development work on this project came the Carrier Engineering Co.'s "Rotodip" plant design and on the chemical processing side the author's company's "Roto-Bonderite" chemicals.

In this method of "Bonderizing" a combination of immersion and spraying techniques is employed. Sprays operate above each tank, bodies are rotated as they pass through each zone and the track of the conveyor is of such a form that besides the drenching bodies receive from the spray system they are completely immersed in the solution in the tank during passage. After processing and drying off, the bodies are dip-primed and subsequently stoved. Thus greasy bodies are passed into the plant and primed bodies are delivered from it.

As far as pretreatment is concerned, the sequence of operations carried out is common to both "Spra-Bonderizing" plants and "Rotodip," namely, cleaning, for which alkali or emulsion cleaners are used, followed by double water rinsing, which may be hot or cold according to circumstances, "Bonderizing," hot-water rinsing, chromate rinsing and drying off.

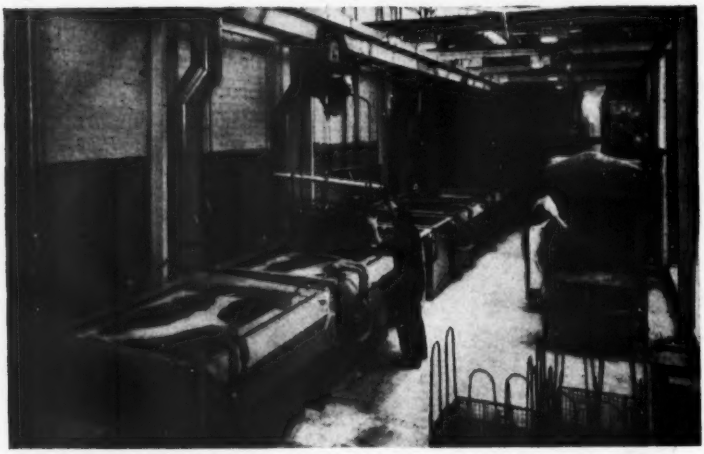


Fig. 4.—Another view of the "Rotodip" plant at Fisher and Ludlow Ltd., through which car bodies are cleaned, "Bonderized," and (dip) primed.

processed separately or in composite fabrications, require more exact control. However, the closer the control of the solution within its limits of loading, strength and operating temperature, the less the likelihood there is of conditions being established which may result in faulty processing.

"Spray Gun Bonderizing"

Not all production is suitable for immersion or spray treatment. On the one hand, the volume of production may be insufficient to warrant the cost of operating such a plant, on the other, the work may be of such a size or of such an awkward shape as to make the handling through a plant impossible. Such production circumstances are met by "Spray Gun Bonderizing" in which the "Bonderite" chemical is applied to the work at room temperature by an ordinary paint-type spray gun. The same general sequence of operations is employed, *viz.*, cleaning, derusting if necessary, spray gun "Bonderizing," rinsing and drying off. Solvent cleaning is most commonly employed with or without the use of an emulsifiable cleaner, and the cleaning is more critical in this case than in the case of immersion in a hot processing solution or spraying by a hot processing solution where a small quantity of residual contamination can sometimes be tolerated.

Brush Bonderite

For touching up, where subsequent fabrication has destroyed the coating and rectification is necessary, a brush "Bonderite" material is available which, as its name implies, is brushed on. Once again, cleaning is necessary before application and rinsing and drying off are necessary after.

Control of Processing Solutions

Solutions are generally very robust and their control is easy, all that is necessary being a simple titration from which the replenishment necessary to maintain strength is a matter of elementary arithmetic. Some solutions which are more complex, as for example, "Bonderite '170'" and "Spra-Bonderite '170'" in which iron, steel, aluminium, zinc and cadmium surfaces can be

Properties of Phosphate Coatings

In composition phosphate coatings are complex mixtures, mainly tertiary phosphates of the heavy metal component or components of the solution, *i.e.*, zinc, and the metal being processed, *i.e.*, iron.

Coatings are heterogeneous and made up of crystals of all sizes, but the mean crystal dimension is dependent upon a variety of factors, the nature of the accelerator or accelerators used, the refining agent, if any, and also upon the method of cleaning used.

Thus, alkali cleaning and pickling will result in a coarse coating in which the mean crystal dimension is high whereas turps wiping or emulsion cleaning will result in a fine coating in which the mean crystal dimension is low.

The absorptive nature of a phosphate coating is such that vapours of water, solvents, oils, etc., in the atmosphere become trapped and retained on exposure to air and in consequence the coating becomes contaminated, thus, in time, its effectiveness can be reduced. But one of its functions is to prevent moisture which may penetrate the paint film from reaching the underlying metal, thus there is a standard recommendation, admirably exemplified by "Rotodip," to paint as soon as possible after drying off.

Phosphate coatings penetrate grain boundaries in the basis metal and, even when the coating is worn away, these traces remain. This is perhaps of no importance in painting applications, but in wear-reducing applications using "Parco-Lubrite" this property can endow treated parts with a self-lubricating characteristic.

Types of Solution

For paint bonding applications the solutions are commonly zinc-phosphate-based mixtures. The reason is that zinc solutions are faster in operation

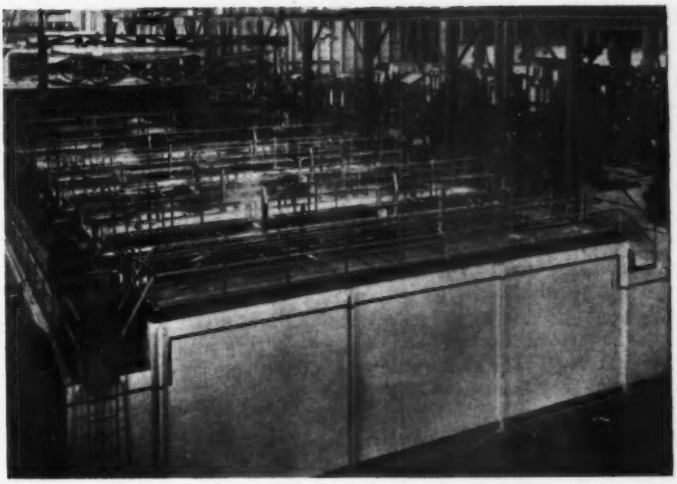


Fig. 5.—View of the "Pylumin" plant at Bristol Aeroplane (Housing) Ltd., through which aluminium bungalows are processed.

than others and, therefore, more suitable to modern production methods where speed is important. They are also less sensitive to temperature and to the other manifold variables which are apt to influence production circumstances from time to time. Corrosion resistance is very good.

Manganese solutions have a slightly higher corrosion resistance but although they can be accelerated they are generally less tolerant in accelerated form than zinc solutions and are consequently mainly used in rust-proofing and wear-reducing applications where processing time is not critical.

Other Aluminium Processes

Considering the alkaline-chromate and the acid-chromate processes, of these, alkaline-chromate processes like "Pylumin" are the simplest to operate and probably the most economical. All that is required by way of plant are mild-steel tanks suitably heated for "Pyluminizing," cold rinsing and hot rinsing. An advantage is that unless the contamination is very heavy, degreasing and processing are combined in the one operation. Processing is carried out at near boiling point (205 to 210° F.).

Acid-chromate solutions like "Bonderite '710' " have the advantage that they can be applied by spraying, by immersion and by brushing. In spray machines and immersion plants the low optimum operating temperature of about 100° F. is an advantage, but stainless-steel equipment is needed in the processing zone which is a disadvantage, and also a prior degreasing sequence of operations is necessary.

The coatings produced are not only different in composition and structure from those produced by the alkali-chromate baths, but their corrosion resistance tends to be inferior. The improvement vouchsafed in paint adhesion is about the same for each type of process.

Anodizing Treatments

Preparation of aluminium cannot be concluded without some reference to anodic oxidation or anodizing. When properly prepared an anodized coating has high corrosion resistance, it is hard and resistant to abrasion, electrically it is a powerful insulator, and it can be used as a base for paint. From the purely decorative point of view, the ease with which the coating can be coloured with organic dyes and pigments is adopted rather than painting. A wide range of attractive effects can be produced, but in the past there were many difficulties attending the task of matching dyed anodized finishes; there was also the problem of light fastness. However, anodized and coloured aluminium hardwear is being featured on some 1956 American cars (neutral-tinted anodized aluminium window mouldings are a feature of the Standard Vanguard III) and it is believed that these disadvantages have been overcome in a new range of dyes now available.

Inevitably in a survey of this kind certain aspects of the subject must be ignored. It is not possible, for example, to go deeply into the conditions imposed by a given application or plant design, into the mechanical-handling problems which may arise, or even into the operating problems which are sometimes encountered. And indeed these things are inclined to be peculiar to a specific application.

From time to time, production developments create a demand for a new process or a novel technique and these are devised sometimes to remain in limited applications, sometimes to expand into general practice. There are, for example, the "Laminate" processes for the treatment of strip from which laminations are to be stamped. These processes exploit the electrical resistance and insulating property of a phosphate coating and represent advances both in the nature of the solution and in the method of application.

(*Continued in page* 36)

Barrel Plating costs

(*Continued from page* 17)

goods. Unfortunately, however, in doing this they often assess their overheads not on the plating shop alone, but on the whole factory. A light engineering firm with a large assembly shop which may have comparatively little expensive equipment, may also have a small plating shop attached to it. In a plating shop the equipment per man is relatively expensive and also this has a high maintenance, so that the overhead on a plating shop will be considerably more than that on a light assembly shop which may work out at, perhaps, 150 to 200 per cent. The manufacturer, however, for his internal convenience, may work out an overhead covering the whole and may, therefore, get a much lower works cost for his metal-finishing work than he would do if he were doing this by itself. If he then compares these costs with the prices quoted by outside firms, he may consider the latter to be high. In some cases manufacturers have been known to state that their works costs were only a small fraction of the cost worked out by an out-plater, although it is quite obvious that the work in question could not have been carried out at the cost they state. On going into the matter it is usually found that the metal finishing department has not been separately costed, but has been run in with some other departments which have much lower overheads and in some cases it may be that the cost of some of the personnel has also been carried on other work. This is often the difficulty where manufacturers having plating shops of their own are dealt with. Occasionally, however, the reverse is found to be true and if the plating shop is associated with, say, a machine shop having a large amount of expensive machinery or possibly, also, in the case of a works very highly systemized, the overheads may be higher than would normally be found in an out-plating shop and the works cost of carrying out a plating process may be quite considerably higher than the price which an out-plater would charge for the same work.

* * * *

It is hoped that the above may stimulate various plating firms into keeping a more careful record of the cost of their processes, even if they do not adopt the system suggested above. There is no doubt that it will be to everybody's advantage if this were done and it must also be remembered that if careful records are kept an examination of these may show how the costs themselves could be materially reduced without, of course, reducing the quality of the work produced. If the out-plater is to survive in the present difficult times, it will be necessary for him to keep his costs as low as possible. At the same time, the prices quoted should always yield a reasonable margin of profit.

The reduction of costs by improvement of the process employed must obviously be the aim of all industrial undertakings as it is only in this way that a better standard of living can be obtained in the country. The out-plater undoubtedly has his share to do in achieving this end, and if he does this there is little doubt that he will benefit himself.

Metal Preparation

(*Continued from page* 35)

Another process of similar character is "Strand Bonderizing" which finds its sphere of usefulness in the wire-drawing industry.

Still thinking in terms of phosphate coatings, when one property of a solution or coating is exploited to meet a special requirement, it is not to be assumed that all properties will be similarly enhanced or even stay constant, as one quality may be obtained only at the expense of another.

Among the subjects omitted are those materials which are intended to achieve a two-fold object. For example, there are those materials originally developed in America during the war for certain special applications and described as wash primers. In this country they are known as etch primers. Most commonly they are two-pack materials which are mixed immediately before use and are designed to etch the surface and to provide a key and prime the surface at the same time.

The use of phosphate coatings can reduce wear on bearing surfaces. In order to allow for working tolerances on machined parts it was necessary to develop a solution in which crystal size would be uniform and consistent. This was attained but the crystal size varies with the method of cleaning and the material being processed. For a given application, therefore, it is necessary to establish that sequence of preprocessing operations which will produce the size of crystals which suit the actual conditions of wear. Thereafter, so long as neither that sequence nor the material are changed the results will be consistent.

In general, with pretreatment and finishing, once a system has been established by which requirements are met, careful control of all variable components within their appropriate limits will insure consistency. If one factor is changed, material, cleaner, pretreatment, organic finishing medium, it may effect the final result. It is thus a wise precaution to check the possible effect of such a new component before establishing it as part of the finishing system.

DETECTION OF POROSITY IN PLATED COATINGS

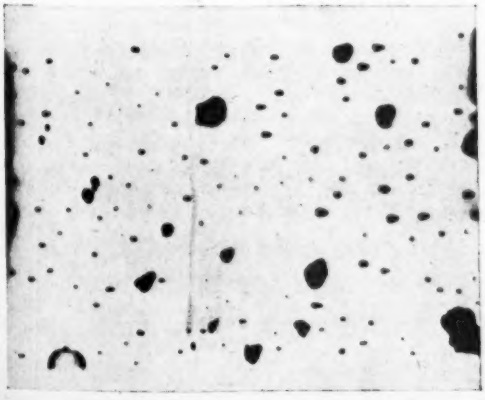
Use of Radiographic Techniques

PORES and other discontinuities seriously impair the quality of industrially produced electroplated coatings, diminishing their effectiveness as protective coatings for metals. Until now it has been difficult to estimate the relative merits of electrodeposits since no generally acceptable method of determining the incidence of such defects was available. Recently, however, the U.S. National Bureau of Standards has developed a non-destructive procedure for ascertaining both the size and position of pores. The method involves photographing an electroplated specimen exposed to radiation.

In earlier research, a technique applicable to plated coatings that have been removed from the basis metal was developed by the Bureau. However, the likelihood of stripped-coating porosity differing from adherent-coating porosity led to further investigation of the problem. The present work was carried out for the American Electroplaters' Society by F. Ogburn of the Bureau staff and Margaret Hilkert of the Society's research fellowship at the Bureau.

In determining the location and size of pores, the specimen, a flat sheet of plated metal a few thousandths of an inch thick, is placed on a photographic film with the coating against the film emulsion. The assembly is held in a cardboard cassette, and the basis-metal side of the specimen is exposed to X-rays or radiation from a radioactive material. To ensure good contrast, the X-radiation used must be soft. This requirement of low-energy X-rays limits the thickness of the basis material to several thousandths of an inch, since thicker metal absorbs too much of the X-ray beam and requires too long an exposure time. Radioactive iron, nickel, or cobalt held against the plated specimen in a cassette are also adequate sources of radiation.

Radiograph of nickel deposit on steel obtained at the U.S. National Bureau of Standards. The large black areas correspond to regions marked as points of reference before plating. Most of the other spots are due to visible gas pits and the smallest dots represent pores.



After a suitable exposure time the film is removed and developed, satisfactory radiographs result from a 3- or 4-min. exposure to an X-ray machine, and from a 24-hour exposure to 1 μc of radioactivity. Wherever a pore existed in the coating, a black spot appears on the developed film. A fine-grain industrial X-ray film gives the most readable radiograph.

This radiographic method detects pits, voids, and inclusions in the coating to the order of 0·001 in. in diameter. Discontinuities in the basis metal may also be determined by radiographing the metal before plating.

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The Nature, Cause and Effect of Porosity in Electrodeposits, II. Radiographic Detection of Porosity in Electrodeposits, by F. Ogburn and M. Hilkert, *Annual Tech. Proc. Amer. Electroplaters' Soc.*, p. 256 (1956).

The Nature, Cause, and Effect of the Porosity in Electrodeposits, by F. Ogburn and A. Benderly, *Plating*, 41, p. 168 (1954).

ACCIDENTS IN THE FINISHING INDUSTRIES

Cases from the Annual Report of the Chief Inspector of Factories

THE Annual Report for 1955 of the Chief Inspector of Factories shows that the steady increase since 1952 in the number of accidents reported continued in the year under review. The finishing and allied industries do not claim a very large percentage of the total number of accidents, although a number of injuries received from specialized causes are described in the report. For example, eighteen non-fatal cases of gassing by the inhalation of trichlorethylene vapour were reported, the year being noteworthy for being the first since 1946 in which no fatal case occurred. The lesson of all these cases and also of a number of other cases where gassing by paint solvent vapours occurred is that particular attention should always be paid to the ventilation of areas where vapour degreasing or paint spraying is being carried out. Particular stress is laid on the danger of using volatile solvents for cleaning etc. in enclosed spaces or under conditions where the heavy vapour can drain into an enclosed space.

Only six cases of lead poisoning in paint and colour works were reported, none of which were fatal, while in the coach-and car-painting industry no cases occurred.

One hundred and two cases of chrome ulceration were reported among workers in chromium plating plants, one particularly heavy incidence being traced to a defective exhaust system due to a fan having been damaged by a falling roof slate.

Abrasion Resistance of Titania-Opacified Enamels

(*Continued from page* 28)

on a piece of mica? If not, then if they would do so and superimpose the results on some of the curves which they had obtained, it would tell a story without words which would be very convincing to the general public.

He would like to know how many plates had been used in the experiments recorded and whether the readings given were the mean of a number and, if so, whether it would be possible to calculate a coefficient of standard deviation giving a figure making it possible to say that one was good, one not so good and one very poor.

Dr. NIKLEWSKI said that they had a measure of other finishes, but it would never go to the public. It would be interesting to measure the abrasion of mica and paint and so on, but they had not done it. On the question of how exact the apparatus was, they had not given any measurement in the paper, but they had been discussing + 5 per cent. In Fig. 4, curves 3 and 4 referred to the same enamel and the curves were very nearly the same. Reproducibility with this apparatus was very good. The two panels to which curves 3 and 4 in Fig. 4 related had been sprayed separately and fired separately, so that small differences between them might be expected. They were satisfied that the apparatus was exact, but the wheels were very important, and if they were used for too long a period it would be no good.

Asked whether the authors agreed that re-facing of the wheels was necessary to get through the skin only, Dr. Niklewski pointed out that in Fig. 4, curve 5 had been obtained without re-facing, and the abrasion was very small. The line was not straight, there being a kink at 6,000 cycles. They had found that re-facing was necessary. The powder from the enamel became embedded, so that refacing had to be done every few thousand times. They did not like doing it, because it reduced the size of the wheels very quickly, and they had very little diameter to play with, but otherwise the results would be erratic. He had used three sets on the work described in the paper.

Overseas Review

(*Continued from page* 18)

Analysis

Two new analytical methods have recently been published to help plating chemists, particularly if they have to control nickel-plating solutions. The first is for the quantitative determination of metallic nickel in conventional nickel plating baths and has been described by F. Brako([6]). This simple direct method, which is claimed to be accurate as well as rapid, is known as the "Sodium Cyanide-Murexide" technique. In essentials, 2 ml. of the sample are pipetted into a flask, diluted with about 400 ml. of distilled water, approximately 0·5 gm. of specially prepared and stabilized murexide indicator added, the mixture swirled until a deep lemon-yellow colour develops and then titrated against standard sodium-cyanide solution to a pinkish-purple end-point. Results show excellent agreement with sodium-cyanide/silver-iodide titrations and it is stated that large amounts of ammonia, nickel chloride, ammonium chloride and boric acid do not interfere. Samples containing large amounts of magnesium sulphate must, however, be treated with a 25-ml. addition of concentrated ammonia before titration with sodium cyanide.

The second is a method described by T. A. Downey([7]) for the volumetric determination of traces of zinc in nickel plating solutions. Basically, analysis consists of two parts:

(1) Extraction and separation of the zinc as a zinc thiocyanate complex into an amyl-alcohol/ether mixture. (This separates the zinc from the nickel solution and any impurities present.)

(2) Complexometric titration of the extracted zinc with ethylenediamine-tetracetate, di-sodium salt. Cadmium is the only impurity found to interfere.

Be Warned!

The use of recorder vans in the streets for detecting the unlicensed operation of radio or television sets has become a generally accepted hazard of present-day piracy. Although the appellation "pirate" has not yet been accorded to those commercial organizations which discharge industrial effluent to the common sewer in inacceptable quantity or quality, it appears that similar steps are being taken to track down their nefarious practices.

Automatic recorders in specially designed trailers rove from plant to plant in the City of Charlotte, N.C., keeping a watchful eye on industrial wastes discharged into the city sewers([8]). These trailers are equipped to make continuous 24-hour tests of plant effluents by continuous measurement of *p*H, flow rate and total volume of flow. Does this foreshadow the shape of things to come in this country?

References

(1) *Iron Age*, 1956, November 8, **178**, (19), pp. 106-109.
(2) *Light Metal Age*, 1956, **14**, (9), (10), p. 24.
(3) *Materials and Methods*, 1956, November, **44**, (5), pp. 104-109.
(4) *Plating*, 1956, **43**, (9), pp. 1134-1142.
(5) *Metal Finishing*, 1956, **54**, (9), pp. 48-55.
(6) ibid. pp. 61-64.
(7) *Plating*, 1956, **43**, (11), pp. 1335-1337.
(8) *Metal Finishing*, 1956 ,**54**, (11), pp. 60-64.

FINISHING

NEWS REVIEW

NO MORE NEED FOR FANS

Ministry approves use of addition agent for suppression of spray from chrome-plating vats

THE surface-active fluorinated hydro-carbon agent, Zero-Mist, which is marketed by the Electro-Chemical Engineering Co. Ltd. of Weybridge, Surrey, has been approved officially by the Factory Department of the Ministry of Labour as a suitable agent for suppressing spray in chromium-plating operations and replacing the fans which were previously obligatory.

As a result of tests carried out, it has been certified that in each test 3 cu. metres of air were taken from above a chromium plating bath and in all cases the analyses showed less than 0·005 mg. of total chromium expressed as chromium trioxide in the atmosphere. The Chief Inspector is consequently proposing to exempt from Regulation 1 of the Chromium Plating Regulations 1931 baths which are treated with an efficient spray-suppressing material.

Scope for Savings

The savings obtained by use of this agent fall under a number of different headings. In general, an exhaust ventilation system, which was obligatory to remove the mist as it is formed, also carries out a great quantity of air which has had to be heated. To carry away the mist formed in a 2,000 gallon tank installation, an exhaust rate of as much as 10,000 cu. ft. per min. may be required with consequent heavy cost, both in capital installation and in the power consumption of the electric motors. Even with the most efficient ventilating systems it was not always possible completely to obviate mist formation, particularly with wide tanks and where there were strong draughts. Also there has always been a strong corrosion problem in the ducts and ventilating system which became coated with condensed corrosive salts. The loss of chromic acid through mist and spray can amount to 30 per cent. of the total acid used, and considerable additional expense has been involved, as well as a health-hazard.

Low Running Costs

Because of the stability of the agent and the fact that it is lost from chromium plating solutions solely as the result of drag-out, its rate of consumption, once the initial addition of the required weight of tablets has been made, is low. It has been estimated that its use on a 1,000 gallon installation for which an 8 h.p. fan would be used would cost little more than half the power cost, plus the cost of raising the temperature from 40°F to 65° F of the 8,000 cu. ft. of air per minute that would be extracted by the fan, assuming that the material would be replaced at the rate of 10 per cent. of the initial quantity per month (which is on the high side).

The use of Zero-Mist during the past few years has been proved to be successful technically but its initial cost has, however, limited its use. The position is now changed by the recent decision to permit fans to be switched off when it is added at the correct concentration to decorative chromium plating baths.

FINISHING LUNCHEON CLUB MEETINGS

THE last meeting of the Industrial Finishing Luncheon Club was held on December 13 when some fifty members were present to hear a talk by Mr. Anthony Hodgetts on "Using Modern Finishes".

The next meeting will be held on February 7 at the usual venue of the Rembrandt Hotel, and on this occasion the Club will be addressed by Mr. A. R. L. Chivers speaking on "The Role of Zinc in Industrial Finishing".

Anyone interested in joining the Club and receiving regular notices of its luncheon meetings should communicate with The Hon. Secretary, Industrial Finishing Luncheon Club, John Adam House, John Adam Street, Adelphi, London, W.C.2.

Vitreous Enamellers adopt New Constitution

AT an extraordinary general meeting of the Institute of Vitreous Enamellers held in London on January 10, a number of resolutions amending the Memorandum and Articles of Association of the Institute were adopted. Following the adoption of the new constitution application has been made to the Board of Trade for a licence to drop the word "Limited" from the official title of the Institute.

The new constitution which was adopted makes no significant changes in the aims or administration of the Institute, but merely falls into line with the requirements specified by the Board of Trade for the granting of the required licence.

A HAPPY AND PROSPEROUS NEW YEAR

The Editors, the Area Managers, and the Staff of METAL FINISHING JOURNAL extend to all readers, advertisers, contributors and other friends in the industry at home and overseas, sincere and cordial good wishes for their happiness and greater prosperity in the year that lies ahead.

BORAX PRICES UNCHANGED

IN August, Borax Consolidated Ltd. announced that they would hold their prices firm in this country from October 1, 1956, to March 31, 1957, unless exceptional factors intervened.

Since then, events in the Middle East have led to an increase in domestic delivery costs here which, although serious, is far overshadowed by the alarming rise in ocean shipping freights.

These factors, coupled with an increase in American domestic and export prices, would normally have meant an increase of £3 to £3 10s. per ton in the company's U.K. prices.

However, in spite of this, Borax now announce that they still intend to hold their prices in the U.K. firm to March 31, 1957, unless altogether exceptional factors make this impossible.

INDUSTRIAL ADVISORY SERVICE

New Organization Set up by National Union of Manufacturers

IN 1953, the National Union of Manufacturers set up, with the help of counterpart funds, an Industrial Advisory Service, and Mr. G. L. Page was appointed industrial adviser. Within 12 months, over a hundred firms had asked for and received help. With further financial assistance from the Board of Trade, the service was expanded and additional industrial engineers appointed, and charges were introduced so that the Service might be self-supporting.

To satisfy this increasing demand and to provide an organization better equipped to deal with it, the National Union of Manufacturers has now set up a new non-profit making company, the National Union of Manufacturers' Advisory Service Ltd., to be known as N.U.M.A.S., which is already operating from its own office at 45/46 St. Paul's Churchyard, London, E.C.1. Telephone: CITy 2135/6.

The chairman of this new company is Mr. Gilbert Salter, chairman of the Midland Council of the N.U.M. The managing director is Mr. G. L. Page.

The N.U.M.A.S. staff will continue the work of the advisory service by providing experienced work-study officers and cost accountants to help carry out agreed schemes of improvement.

The N.U.M.A.S. senior staff of industrial advisers are prepared to visit any firm, irrespective of size, to discuss and report on such matters as organization structure, finance, marketing and distribution, management accountancy, materials control and production. Preliminary discussions are free, subsequent services being charged for according to the extent of the work.

PRODUCING POLISHING PLATES

To meet the demands of the sheet polishing section of BX Plastics Ltd. the company have installed new plating shops to produce polishing plates with an excellent mirror finish.

The normal production methods for cellulosic and vinyl sheet result in the material having surface blemishes and to obtain the mirror finish often required in these products, it is necessary to press the individual sheets between highly-polished nickel plates at elevated temperatures.

After plating the sheets are buffed to achieve a mirror finish.

CORROSION OF METALS IN BUILDINGS

Forthcoming Symposium

THE Corrosion Group and the Road and Building Materials Group of the Society of Chemical Industry are arranging jointly a Symposium on Corrosion of Metals in Buildings to be held at the Institution of Civil Engineers, Great George Street, London, S.W.1, on Thursday, March 21, 1957, from 9.30-6 p.m. The papers to be presented are: "The Resistance of Non-ferrous Metals to Corrosion in Buildings", by F. E. Jones; "The Corrosion of Ferrous Metals in Buildings", by J. C. Hudson and F. Wormwell; "Corrosion of Metals in Contact with Concrete", by P. E. Halstead; "Aluminium Cladding of Buildings", by E. H. Laithwaite and E. W. Skerrey; "The Performance of Zinc and Zinc Coatings in Buildings" by R. W. Bailey and H. G. Ridge; "The Behaviour of Copper in Buildings", by S. Baker and E. Carr.

Preprints of the papers, further particulars and forms of registration may be obtained from the Society of Chemical Industry, 14, Belgrave Square, London, S.W.1.

WOLF TOOL SERVICE DEPARTMENT MOVES

TO provide a better repair service to tool users in the Home Counties, Wolf Electric Tools Ltd. have moved its head service department from 239 Acton Lane, London, W.4, to larger premises at Newlon Works, off Stanlake Villas, Stanlake Road, Shepherds Bush, London, W.12. Telephone No.: SHEpherds Bush 4414/5/6.

The department, controlled by Mr. C. S. Butcher, general service manager, consists of an entirely new two-storey office block together with separate repair workshops in which modern repair equipment is installed.

TRADE and TECHNICAL PUBLICATIONS

"Jenolite News": The December issue of this journal published by Jenolite Ltd., 13-17 Rathbone Street, London, W.1, gives details of a new service that the company are operating. This is the entire pre-treatment of all types of steel products at a new installation at Hanworth Air Park.

Information is also given about the company's new research laboratories which are now complete, and in the design of which are incorporated many novel features.

A complete list is given of the Jenolite Group of Companies and all their products.

"Finishing Facts": The December issue of this magazine published by Imperial Chemical Industries Ltd., Paints Division, Slough, deals with three main subjects. They are: "Colour at the Motor Show", "Why Not Flowcoating?" and "Paints for High-speed Aircraft".

The article on flowcoating by Mr. D. W. Hislop, B.Sc., compares the process with more widely established methods of paint application and discusses the factors that are likely to govern its adoptions by industry.

"The Heat-Treatment Journal": In the December issue of this journal published by Wild-Barfield Electric Furnaces Ltd., Elecfurn Works, Otterspool Way, Watford By-Pass, Watford, is the concluding chapter of an article dealing with spring heat treatment and finishing. The article concludes by looking forward to an installation that will automatically feed low-carbon steel springs into a conveyor furnace, carburize, diffuse, transfer to a lower temperature zone and then quench in an austempering bath.

"The Painting of Aluminium": A leaflet has been produced by British Paints Ltd. in which it is stated that one of the main difficulties in painting aluminium is in obtaining good adhesion to the very smooth surface of rolled sheets by the priming paints making some form of etching treatment necessary.

It is important that priming coats should not contain lead or graphite pigments because either is liable to set up galvanic attack on the aluminium.

The leaflet gives a recommended procedure for painting and discusses the company's products that are most suited to it.

"Photoelectric Temperature Control": Elcontrol Ltd., 10 Wyndham Place, London, W.1, have produced a brochure describing a photoelectric temperature-limit switch which can be used for switching off the heating current when the temperature of the work piece has risen to the desired limit, in such applications as heat-treatment, resistance welding, etc. It also describes their photoelectric controller which provides on-off switching at predetermined temperatures allowing a given temperature to be maintained. Both instruments incorporate a separate viewing which can be used in any convenient position remote from the main control cabinet.

"The Aluminium Courier": The December issue of this journal published by the Aluminium Development Association, 33 Grosvenor Street, London, W.1, contains articles on aspects of aluminium usage.

One article deals with the cleaning and maintenance of aluminium and gives information on those alloys having good weathering properties and so being especially suitable for architectural applications. There is also the fourth article in a series which deals with extruded sections and assemblies.

Another well-illustrated article explains the uses being made of aluminium for shop fronts and fittings. There are many photographs showing current British, American and Continental practice, which include fascias, panellings, window-display fittings, counters, interior shelving, roller shutters and blinds, grilles, light fittings, small trolleys and ladders.

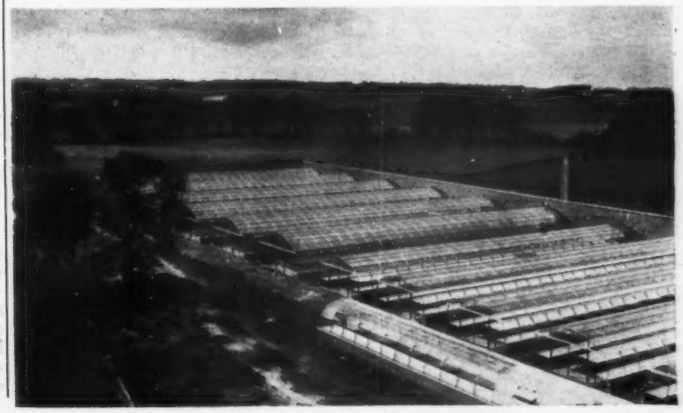
"Water Treatment for Industry": This booklet published by the Imperial Chemical Industries Ltd., Alfloc Water Treatment Service, 4 Cromwell Place, South Kensington, London, S.W.7, outlines the points that need consideration when dealing with an industrial water-treatment problem.

The impurities that may be found in water are listed; difficulties which these impurities may cause are explained; and various methods of filtration, softening and chemical conditioning are described.

The Alfloc technical service is explained in which the company's technical representatives will help with water problems and survey the plant and water conditions and, if necessary, select samples for further examination in the laboratories. The information collected is studied and recommendations for overcoming the problem are forwarded in the form of a comprehensive report.

This new nursery for the Leeds Corporation Park Department opened recently at Red Hall, Shadwell, Leeds. The nursery covers one and a quarter acres, and comprises fifteen glasshouses flanked by an ancillary building containing offices, etc.

The glasshouses, built by V. and N. Hartley Ltd., are of aluminium construction, and although aluminium is widely used unpainted, in this case it was decided to stove-enamel the metal. The stove-enamelling supplements the durability of the aluminium and affords extra protection against the injurious mercury and copper salts sometimes contained in insecticides. The glazing bars—which like all the other twenty or more extruded sections used in the houses are made of Noral 50S alloy, supplied by Northern Aluminium Co. Ltd.—are designed to support an entirely new glazing system that uses a polyvinyl-chloride cushioning on all four edges of each pane of glass, thus making it shock-, draught-, and water-proof.



COATINGS MEETINGS TO BE HELD IN CANADA

THE 11th divisional conference of the Protective Coatings Division of The Chemical Institute of Canada will be held in Toronto, February 12, 1957, at the Seaway Hotel, and in Montreal, February 22, 1957, at the Ritz Carlton Hotel. The same programme is scheduled for both cities. The speakers will include: W. M. Kraft, "Considerations in the Processing and Uses of Pentaerythritol Alkyds"; J. K. Hossack, "New Developments in Inorganic Coatings;" W. N. B. Armstrong and J. M. Suggitt; "Coatings Evaluation and Laboratory Correlation with Field Experience"; R. R. Hunter, "Coatings for High Speed Aircraft"; and W. B. Anderson, "The Properties and Uses of Some Organic Compounds of Titanium". A. J. Lilly, manager of aircraft sales, Canadair Ltd., Montreal, is to be the luncheon speaker at both sessions.

PROGRESS IN NICKEL MINING EXPANSION

Developments in N. Manitoba

THE flow of materials and supplies for the recently announced $175,000,000 nickel development in Northern Manitoba is now being organized. Pending construction of the Canadian National Railway spur, movement of freight to the plant and mine sites will be made by tractor train throughout the winter so that construction may be pushed forward vigorously in the spring.

Ralph D. Parker, vice-president and general manager of Canadian Operations, who was elected a director of the Company on January 7, recently announced appointments in the newly created Manitoba Division of The International Nickel Co. of Canada, Ltd., as follows: manager, James C. Parlee; assistant manager, F. F. Todd; assistant manager, S. A. Crandall.

The company have opened a Winnipeg office, occupying the third floor of the Royal Trust Building, 436 Main Street, where Mr. Parlee will make his headquarters during the construction period.

THE TREATMENT OF TRADE WASTE

One-day Symposium in Birmingham

The Institute of Sewage Purification (Midland Branch) is holding a one-day symposium on Trade Waste Treatment in the new Mechanical Engineering Lecture Theatre, University of Birmingham, Edgbaston, Birmingham 15, on April 9, 1957 at 9.15 a.m. Dr. Arthur Key, F.Inst.S.P., senior chemical inspector, Ministry of Housing and Local Government, will be Chairman. The official opening of the symposium will be performed by the Chairman of the Birmingham, Tame and Lea District Drainage Board, Alderman A. Paddon Smith, J.P. Papers will be presented as follows: "Problems Concerned with the Acceptance of Trade Effluents into Public Sewers", by M. A. Kershaw, F.C.S., F.I.P.H.E., F.Inst.S.P. "Obligations of Local Authorities and Traders under the Rivers Pollution Prevention Acts", by M. Lovett, B.Sc., F.R.I.C., F.Inst.S.P.; "Treatment of some Industrial Organic Wastes", by D. H. Sharp, Ph.D., B.Sc., A.R.I.C.; "Acid Wastes and their Neutralization", by S. H. Jenkins, D.Sc., F.R.I.C., F.Inst.S.P., and C. H. Hewitt, A.R.I.C., M.Inst.S.P.; "Treatment of Plating Wastes and Cyanides", by A. E. J. Pettet, M.A., F.Inst.S.P.; and "Gas Works Effluents and their effect on Sewage Treatment", by W. T. Lockett, M.Sc., F.C.S., F.Inst.S.P.

NO LET-UP IN NICKEL SHORTAGE

U.S. view stated in Congress

FEARS that supplies of nickel were being diverted from the defence stockpile to industry led to a survey being made into the supply and distribution of nickel in the U.S. Now, Mr. Weeks, U.S. Secretary of Commerce, has told Congress that it may be 1960 or even 1965 before the present shortage is relieved. The supply of primary nickel available would not meet the nation's full requirements for several years, he said. The expansion of the free world supply now under way or definitely planned might meet the U.S. need fully by 1960-65—when such expansions were due to materialise.

Mr. Weeks added that there should be a fair and equitable distribution of available supplies for non-defence purposes, and a co-operative understanding in the industry would be preferable to Government control of distribution.

"It is abundantly clear that the inadequate supply of nickel for all purposes has retarded and is retarding industrial expansion in several areas", he concluded.

NEWS IN BRIEF

At the Annual General meeting of the Sheet and Strip Metal Users' Technical Association, held in London earlier this month, a special resolution was adopted changing the name of the Association to the Institute of Sheet Metal Engineering. Mr. W. E. Wright, director of the Pyrene Co. Ltd. and a founder Council Member of the Association, was elected an Honorary Vice-President.

* * *

The Corrosion Group of the Society of Chemical Industry is to hold another in the series of successful conversaziones, on January 24 in the Battersea Polytechnic, London, commencing at 6.30 p.m. A small exhibition will be staged and technical films will be shown during the evening. Buffet supper will also be available.

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Owing to the number of applications considerably exceeding the numbers which could be accommodated on the first visit, a further visit has been arranged by the Midland Branch of the Institute of Metal Finishing to the works of John Summers and Sons Ltd., Shotton, Cheshire. This visit is to take place on January 24.

* * *

A reception at the Dorchester Hotel, London, for the Press and executives in the metal industries marked the opening of the new Feltham (Middlesex) works of Eutectic Welding Alloys Company, Limited. Mr. A. J. Speakman, deputy director of the British Productivity Council, was the principal guest and both he and Mr. R. D. Wasserman, governing director of the company, addressed the guests. The latter explained that the firm came to this country five years ago, following pioneer work on the Continent and America in relation to the supply of materials for, and providing technical instruction in, low-heat-input welding. Examples were exhibited of welding repairs carried out with the company's products and processes on various components, including iron and non-ferrous castings.

Cleaning and Protection of Motor-car Body Components

Use of a process developed by E. Spiero Chemicals Ltd.

THE rapid growth of fully automated production and assembly in the motor-car industry has made it necessary to use continuous automatic finishing plants for car bodies. As a result of this, components containing faults cannot be rectified on the final process and have to travel to the end of the line where they are dealt with by hand methods.

In car-body manufacture, components tend to rust after pressing and before assembly by welding, etc., and thus there is a need in this stage of production to protect the components against corrosion during stoppage and for subsequent assembly.

In some cases, components may be deep phosphated and primed prior to assembly, but the deep-phosphate coating makes subsequent spot welding a difficult operation.

In many cases, therefore, it is advantageous to install degreasing, derusting, and protective processes for metal components prior to assembly so that fully automatic and efficient finishing may be carried out when, for instance, the body is complete. By adopting this procedure it is possible to ensure that the final finishing processes are not marred by defects arising from corrosion, etc., which has taken place earlier in the production sequence.

An example of the application of a cleaning process early in a body production line is that installed at the Longbridge, Birmingham, works of the Austin Motor Co. Ltd. by E. Spiero Chemicals Ltd. The process consists of degreasing, deoxidizing, neutralizing and oiling.

Operation of Process

The body pressings are first placed in an emulsion-type degreaser, used cold. Any type of container can be used for this solution, the immersion time of the components depending upon the degree of contamination of the solution. Following this the components are thoroughly water rinsed and then passed to a lead-lined tank containing a deoxidizing solution, which is used at a temperature of 170° F. This solution is an efficient rust remover and is rapid in action. Following this treatment and after rinsing, the components are transferred to a neutralizing solution contained in a stainless-steel tank. This solution is also operated at 170° F and, in addition to neutralizing the surface, it deposits a thin phosphate coat on the components, the thickness of the coating being sufficient to give the temporary protection against corrosion required at this stage.

From the neutralizing solution the components are then conveyed into a steel tank containing dewatering fluid which in addition to its dewatering action deposits an oil coating on the surface of the components.

Control of Solutions

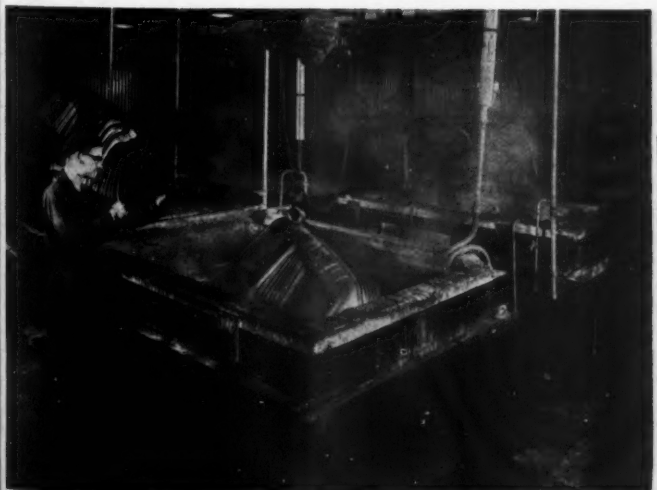
Control of the solutions is easily carried out using special test equipment supplied by the company.

The degreasing and cleaning solution is non-toxic and the installation costs are very low. As this solution has a very low surface tension it is economical in use and also has no chemical action on either ferrous or non-ferrous metals. The de-oxidizing solution is supplied in powder form and is chemically inert in this condition. The solution causes the least attack necessary on the base metal and in use no spray or fume is evolved.

The phosphate coating deposited is thick enough to provide the degree of protection required, but is thin enough to allow spot welding to be used during subsequent assembly of the components, a method not practicable after deep phosphating.

The process as a whole is especially advantageous in relation to automation, as it ensures that when the components are finally processed or finished, rejects are reduced to the absolute minimum.

Body components being treated by the Spiero process at the Longbridge Works of the Austin Motor Co. Ltd.



MIDLAND ENAMELLERS' ANNUAL DINNER

The Midland Section of the Institute of Vitreous Enamellers staged its Annual dinner at the Station Hotel, Dudley, on the evening of January 11. Some seventy members were present to hear the toast of the Institute proposed by Mr. S. W. Vickery, chairman of the recently formed Vitreous Enamel Development Council. Mr. G. H. Legg, chairman of the Midland Section, responded on behalf of the Institute and welcomed the guests who were present.

TECHNICAL AND INDUSTRIAL APPOINTMENTS

Dr. H. G. Taylor is to become director of the **Electrical Research Association** in succession to the late Dr. S. Whitehead, the appointment to take effect from April 1. Dr. Taylor was educated at Taunton School, Plymouth and Devonport Technical College, Barrow-in-Furness Technical College, Battersea Polytechnic and City and Guilds Engineering College, and received his practical training with Vickers Ltd. and Metropolitan-Vickers Electrical Co. Ltd. After serving for 8½ years (from 1931-39) as technical assistant with the Electrical Research Association, he was electrical engineer to the Copper Development Association for 5½ year and then manager of the Industrial development department of Philips Electrical Ltd. For the past nine years, up to the present time, he has been director of research of the British Welding Research Association.

* * *

Ralph D. Parker, a vice-president of **The International Nickel Co. of Canada Ltd.,** has been elected a director of the company.

He succeeds James S. Duncan, C.M.G., who has resigned from the board in connexion with his recent appointment to the post of chairman of the Hydro-Electric Power Commission of Ontario.

* * *

British Titan Products Co. Ltd. announced that Dr. G. I. Higson has relinquished his appointments as a director and chairman of the company.

Mr. G. H. Beeby, who succeeds him as chairman, was formerly chairman of the Salt Division of Imperial Chemical Industries Ltd. and has been a director of British Titan Products Co. Ltd. since March, 1948.

* * *

Mr. R. T. de Poix has been elected chairman of the **Zinc Development Association** for 1957. Mr. de Poix is the Managing Director of Henry Gardner and Co. Ltd. and represents the Canadian zinc producers—the Consolidated Mining and Smelting Co. of Canada Ltd. and the Hudson Bay Mining and Smelting Co. Ltd.—on the Council of the Association.

MEETINGS OF THE MONTH

JANUARY 17

Institute of Metal Finishing (Midland Branch). Dinner and Dance, Grand Hotel, Colmore Row, Birmingham, at 6.45 for 7.15 p.m.

JANUARY 21

Institute of Metal Finishing (London Branch). "The Chromium Plating of Gun Barrels", by R. A. F. Hammond, B.Sc., A.R.C.S., F.R.I.C., at the Northampton Polytechnic, St. John Street, London, E.C.1, at 6.15 p.m.

JANUARY 24

Institute of Metal Finishing. Works Visit to John Summers and Sons Ltd., Shotton, Chester.

JANUARY 25

Institute of Metal Finishing (Sheffielding and North-East Branch). General Debate on plating problems with J. H. Woods in the chair at the Grand Hotel, Fitzwilliam Room, Sheffield, at 7 p.m.

JANUARY 31

Institute of Vitreous Enamellers (Midland Section). "The Effect of Mill Additions on the Properties of the Vitreous Enamel Finish", by G. A. Greenwell, at the Birmingham Exchange and Engineering Centre, Birmingham, at 7.30 p.m.

FEBRUARY 5

Institute of Metal Finishing (Midland Branch). Joint meeting with the Organic Finishing Group. "Organic Finishing of Electro-deposited Coatings—Zinc Plate", by P. Costelloe, at the James Watt Memorial Institute, Great Charles Street, Birmingham 3, at 6.30 p.m.

FEBRUARY 13

Institute of Metal Finishing (Scottish Branch). Buffet and Dance at Burlington House, Bath Street, Glasgow, 7.30 p.m.

FEBRUARY 14

Oil and Colour Chemists' Association (Scottish Section). "Alkyd Architecture", by R. A. Brett, B.Sc., at More's Hotel, India Street, Glasgow, at 7.15 p.m.

FEBRUARY 15

Institute of Metal Finishing (Sheffield and North-East Branch). Dinner and Dance at the Grand Hotel, Sheffield, at 7 p.m. for 7.30 p.m.

FEBRUARY 16

Oil and Colour Chemists' Association (Scottish Junior Sub-Section). "Stoving Finishes", by Mr. Rogers, B.Sc., at More's Hotel, India Street, Glasgow, at 10 a.m.

FEBRUARY 18

Institute of Metal Finishing (London Branch). "Soldering of Metallic Coatings", by G. L. J. Bailey, Ph.D., D.I.C., F.Inst.P., W. Marchand, A.R.I.C., and C. J. Thwaites, B.Sc.(Eng.), A.R.S.M., at the Northampton Polytechnic, St. John Street, London, E.C.1, at 6.15 p.m.

FEBRUARY 22

Institute of Metal Finishing (Sheffield and North-East Branch). "Difficult Plating Processes as Typified by the Electrodeposition of Manganese and Aluminium", by Professor J. W. Cuthbertson, D.Sc., F.I.M., A.M.I.E.E., at the Grand Hotel, Fitzwilliam Room, Sheffield at 7 p.m.

Mr. J. O. Lay, who has recently been appointed chief research chemist of the **Jenolite Group,** is now in charge of the company's new laboratories.

* * *

Mr. Tom Bishop, B.Met.(Hons.), F.I.M., has relinquished his positions as Metallurgical Editor of *Iron and Coal Trades Review* and Editor of *Metal Treatment and Drop Forging*. He has joined the metallurgical staff of **John Miles and Partners (London) Ltd.,** consulting engineers for metallurgical industries, of 76 Cannon Street, London, E.C.4. Mr. Bishop was with Industrial Newspapers Ltd. for over 10 years. He received his degree at the University of Sheffield in 1939, his Associateship of the Institution of Metallurgists in 1947, and subsequently his Fellowship in March, 1954.

It has been announced by Cellon Ltd. that Mr. N. F. Rose has been appointed vice-chairman of the associate company **Merry and Minton Ltd.,** Northfields, Birmingham, while Mr. R. J. Ledwith and Mr. E. C. Mulford have been co-opted to the board of that company. Mr. Rose is a director of both companies; Mr. Ledwith and Mr. Mulford are respectively chief chemist of Cellon Ltd. and works manager of Merry and Minton Ltd.

* * *

The appointment of Mr. J. Kay as representative for the West of England has been made by **Martonair Ltd.,** Richmond, Surrey, manufacturers of pneumatic hoists, cylinders, control valves and accessories. Mr. Kay was previously a member of the technical staff at the Richmond head office.

Latest Developments in PLANT, PROCESSES AND EQUIPMENT

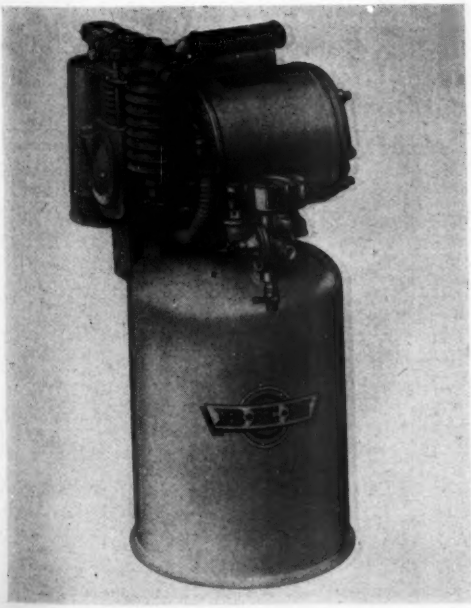
Oscillating Hoists

A SERIES of automatic, oscillating hoists, has been introduced by Martonair Ltd., Parkshot, Richmond, Surrey. The hoists are intended for applications where it is necessary for the load to be automatically oscillated as for example, on removal from oil, water and brine quench treatment tanks, or from degreasing and other surface treatment baths. These hoists have all the features of standard Martonair hoists—minimum headroom, low maintenance due to the absence of high-speed components, minimum consumption (air is used only when lifting), and the hoists cannot be damaged by overloading. Check valves prevent the load dropping if the air supply fails. When operated on manual control, variable speed may be obtained depending on the amount that the control valve trigger is depressed, together with the balance effect, whereby the load may be raised a few inches manually for each positioning without recourse to the control valve.

The magnitude and position of oscillation is completely variable, such that any length of oscillation can be achieved at any position of the lift within the maximum capacity of the hoist, and is obtained by the adjustment of the two trips mounted on the side of the piston. Speed of oscillation is variable for both raising and lowering by means of a pair of air flow regulators, which are incorporated. The normal maximum speed on both lowering and raising is 1 ft. per second. The number of oscillations depends upon both speed and magnitude, and, with an oscillation of 1 ft. at the maximum speed, 30 oscillations per minute would be obtained. A standard type of hand-control valve is also fitted which enables the hoist to be fully raised or lowered in the usual manner. Change over from hand control to automatic oscillation is obtained by a chain-operated selector valve.

The hoists are available with double eyebolt mounting, or with the normal range of Martonair 4-wheel articulated trolley sets.

Fig. 1.—Air Compressor.



Air Compressor

A NEW model has been added to the comprehensive range of air compressors produced by B.E.N. Patents Ltd., High Wycombe, Bucks. It has been developed to meet the demand for a source of compressed air where a small volume is required at pressures up to 50 lb. per sq. in. such as beer lifting, temperature control, etc.

Weighing approximately 98 lb. the unit is self-contained and comprises a single-cylinder air-cooled compressor—2 in. bore x 1 in. stroke—with a displacement of 1·7 cu. ft. per minute direct coupled to an electric motor of 1/3 h.p.

Fully automatic control is arranged by means of an electro-pneumatic pressure switch and the motor is protected against overheating by a special thermo-trip cut-out device.

Cooling is by means of a finned expansion chamber and the machine is fitted with air-intake filter, silencer, air-pressure gauges, adjustable relief valve and a pressure-regulating valve.

It is mounted (Fig. 1) on an air receiver 12 in. x 15 in. with a capacity of 1·25 cu. ft. The unit is claimed to be smooth running, silent in operation and portable.

Chemical Sealer

IT has long been recommended by Jenolite Ltd., 13-17 Rathbone Street, London, W.1, that the treatment of steel work by their rust remover and neutralizer process should be followed by the application of one of a range of chemical sealers marketed by the company. An addition to the range of sealers was recently announced. The new

sealer, code CS.14, has been evolved over a long development period for use in highly corrosive environments. The sealer, which differs entirely from the earlier products in the range, is based on a rubber modified epoxy resin and is said to possess extremely high resistance to almost every corrosive influence to which steel work can be subjected. It is claimed that this sealer is impervious to moisture and proof against attack by both acids and alkalis. It is unaffected by ketones and by mixed aliphatic hydrocarbons. Initial curing takes place in twenty-four hours after which it can be painted with any type of primer or paint. Full strength and flexibility is achieved by the coating after seven days.

Automatic Gas Burners

A RANGE of high-efficiency gas burners has been introduced by G. R. Gilbert Ltd., Hackbridge Road, Hackbridge, Surrey. Three main sizes are available with capacities approximately equal to 1½, 3 and 5 gallons of oil per hour. They can normally fire into the same furnace as the oil burner and so be used as a permanent feature or a reserve burner.

The provision of an adjustable stand for the unit, plus a burner feed that can be extended from a minimum of 8 in. up to 36 in. and if necessary, bent, enables these units to be used almost anywhere. (Fig. 2.)

They will use town's gas of 450 B.Th.U. or more, at a minimum of 2½ in. WG. A fan is direct-coupled to a scientifically-designed mixing chamber in which the gas is intimately mixed with sufficient air to ensure correct combustion. Flame heads are designed to make full use of the high velocity gas and air and still to retain a stable flame which neither lifts off at maximum aeration nor lights back when shut down to very low gas rates.

Fitting entails the provision of a gas feed of suitable size and connecting it to the electricity supply. If an oil burner is in use it is possible to change the wiring over from one unit to the other. Electric thermostats are used for temperature control.

On the smallest fully automatic unit a thermo-electric combustion protection device is fitted. Lighting procedure is as follows: Turn on the main gas cock; lift the pilot-control button, hold it up and light the pilot; and when the pilot has been on for a short while release the button and switch on the fan motor.

Fume Removal Fans

THE Series 2 range of "Tornado" rigid PVC fans for the removal of corrosive fumes was made available by Keith Blackman Ltd., Millmead Road, London, N.17, a few months ago. These fans produced in collaboration with Tanks and Linings Ltd., Droitwich, have capacities up to 40,000 cu. ft. per min. and pressures up to 4 in. w.g.

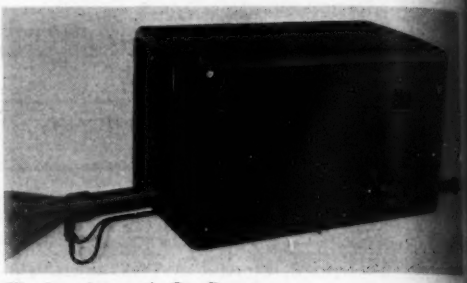


Fig. 2.—Automatic Gas Burner.

The company has now announced that the Series 1 range is now on the market. Fans in this range are smaller, with a fume handling capacity of 50 to 180 cu. ft. per min. at pressures up to 1·25 in. w.g. and are direct driven by a totally enclosed 400/440 volt electric motor.

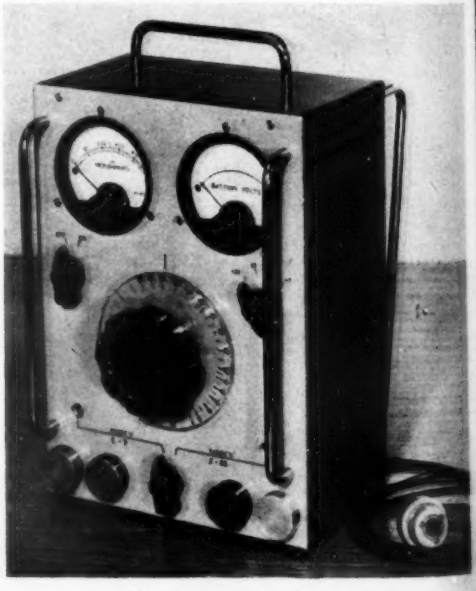
Metal Sorter and Resistivity Measurer

A PORTABLE battery-operated instrument for sorting and identification of non-ferrous metals and alloys has been introduced by The Solartron Electronic Group Ltd., Thames Ditton, Surrey.

The basic design of the Solartron metal sorter and resistivity test set, Type MM 611, originated from The British Aluminium Co. Ltd. It is a practical instrument for use by storekeepers, fitters, foundrymen, toolmakers, press operators, etc., with little or no electrical or electronic knowledge.

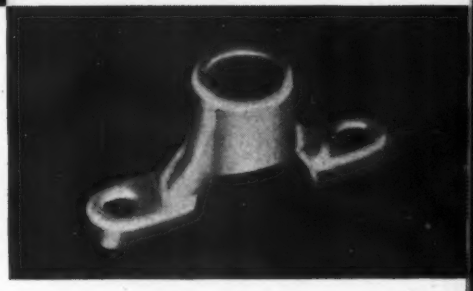
(*Continued in page* 48)

Fig. 3.—Metal Sorter.



NOT TOO SMALL

For Hot Galvanizing



Through modern pre-occupation with the large and spectacular, we often forget the vital importance of the little things—the nails, washers, nuts and bolts which keep the parts together. These, not less than the main steel structures need hot galvanizing—the best way of ensuring long-term protection at a reasonable cost. Few articles are too small to be treated. Up-to-date methods of centrifugal galvanizing allow small parts to be given a heavy and uniform coating of zinc. Threads as fine as those on a 5/16″ diameter bolt can be galvanized ready for use—with no subsequent cleaning required. Whatever the size of a part, large or small, it can usually be galvanized.

Hot Dip Galvanizers Association

The Hot Dip Galvanizers Association, a non-trading body, welcomes enquiries. Write to 34 Berkeley Square, London, W.1
Tel. Grosvenor 6636

Member of the Zinc Development Association

Plant Processes and Equipment

(*Continued from page* 46)

The instrument (Fig. 3) is operated by dry batteries and consists of an investigating head on a lead, which is plugged into a small instrument case. The test heads are interchangeable and designed to ensure that changes of ambient temperature do not cause drift.

The head is placed on the metal surface, which need not, necessarily, be flat, and identification is based upon the specific resistivity of the particular metal.

Provided the metal or alloy has a specific resistivity between 1·0 to 28·0 micro-ohms per centimetre cube, it may be measured, or, inversely, the metal or metals distinguished or sorted.

Four metal standards are provided below the calibrated dial, by means of which the instrument's calibration may be checked and the necessary correction made by the control on the panel.

The many uses of the instrument include: sorting metals and alloys; quick and accurate measurement of electrical resistivity; detection of the clad side of rod, sheet, tube and bar, whether as a raw material or partly or fully fabricated; inspection of the uniformity of cladding, coatings, etc.; detection of local variations in hardness; surface flaws, or embedded foreign matter; and the testing, from one side only, for variations of thickness, within certain limits.

There is no upper limit to the size or complexity of shape of the metal structure to be examined for any of the above data. The minimum requirements are that the metal surface must be sensibly smooth, but need not be flat, and the test portion should have a minimum diameter of 0·75 in. and a minimum thickness of 0·02 in.

Fig.4.—Demonstration of effectiveness of dewatering lacquer coating.

De-watering Lacquer

THE introduction of "Water-White" de-watering lacquer was referred to in thise pages in the May 1956 issue. Further evidence of the protective properties of this lacquer is afforded in Fig. 4. This illustrates a piece of mild steel sheet of which the left-hand portion was lacquered while wet and then exposed to weathering for a fortnight. The result shows the lacquered portion to be unaffected, while the untreated portion has rusted.

This new lacquer, which can be applied to products as they come direct from the cold water swill, is manufactured by Tool Treatments (Chemicals) Ltd., Birmingham Road, West Bromwich.

New Range of Barrelling Equipment

THE availability of a range of barrel de-burring and finishing equipment offering a number of different models of barrel finishing machines and all necessary equipment, compounds, and abrasive chips, was referred to in these pages in last month's issue. This equipment has been developed by the Almco Division of Queen Stove Works Inc., Minn., U.S.A., who are represented in this country by Almco Supersheen Division of Great Britain Ltd., Hitchin, Herts. Owing to a typographical error the name of the company was unfortunately mis-spelt in the original reference.

Pressurized Degreasing Unit

A DEGREASANT which removes heavy contamination of grease and oil by converting them into soluble soaps is marketed by Dee Chemical Proprietaries Ltd., Spencer Road, Belper, Derbyshire, under the name of Jizer. This material is neither acid nor caustic and is not a solvent in the normal sense of the word. It operates by converting greasy or oily residues into soaps, which are soluble in water or seawater, and can therefore be quite simply flushed away by a water wash.

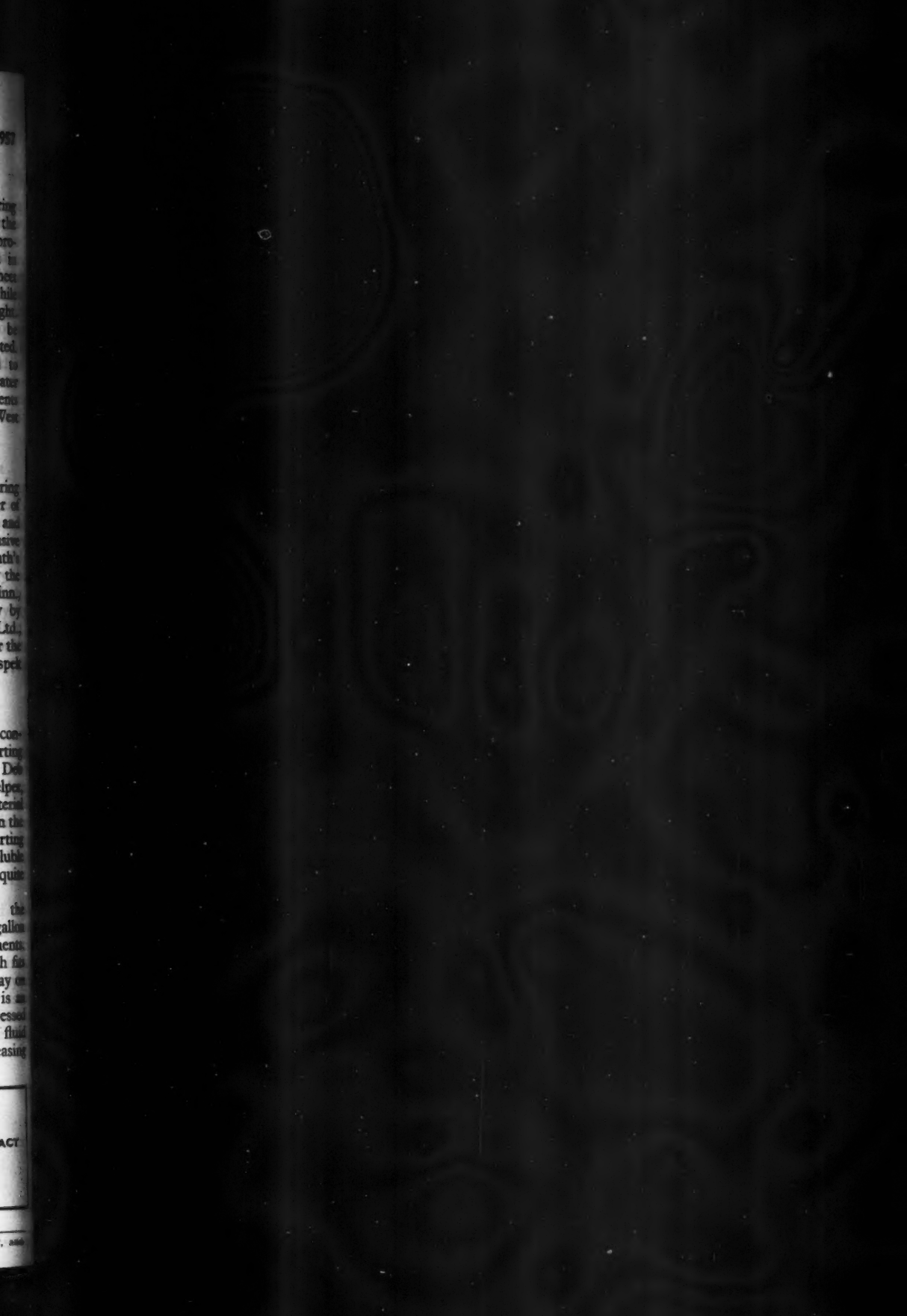
The company has recently announced the availability of a small degreasing unit of six gallons capacity for the degreasing of small components. This unit consists of a steel bucket into which fits a galvanized wire mesh basket fitted with a tray on which the components rest. Below the tray is an agitator unit which is connected to a compressed air supply, this produces a turbulence of the fluid round the parts and accelerates the degreasing operation.

Analysis of Electro-Plating Solutions

FOR A QUICK AND ACCURATE SERVICE CONTACT

FULNECK LABORATORIES

FULNECK, PUDSEY, Near LEEDS,

Telephone: PUDSEY 4011

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